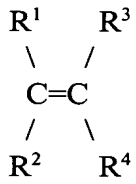
transferable atom or group, and a catalyst system comprising a transition metal compound which participates in a reversible redox cycle with said initiator or a dormant polymer chain end, and a ligand to form a (co)polymer, [the transition metal compound being capable of participating in a redox cycle with the initiator and a dormant polymer chain], and the ligand being any N-, O-, P- or S- containing compound which can coordinate in a σ-bond to the transition metal or any carbon-containing compound which can coordinate in a π-bond to the transition metal, such that direct bonds between the transition metal and growing polymer radicals are not formed, wherein said transition metal compound and said ligand are matched with one another in order to provide reaction with said initiator to reversibly generate a radical.

5. The process of Claim 1, wherein said monomer(s) are of the formula:



wherein R^1 and R^2 are independently selected from the group consisting of H, halogen, CN, CF_3, straight or branched alkyl of from 1 to 20 carbon atoms, α,β-unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms, α,β-unsaturated straight or branched alkenyl of 2 to 6 carbon atoms substituted with [a] halogen, C_3-C_8 cycloalkyl, phenyl which may optionally have from 1 to 5 substituents on the phenyl ring selected from the group consisting of C_{1-6}-alkyl, C_{1-6}-alkenyl, C_{1-6}-alkoxy, halogen, nitro, carboxy, C_{1-6}-alkoxycarbonyl, hydroxy protected with a C_{1-6}-acyl, cyano and phenyl, heterocyclyl, $C(=Y)R^5$, $C(=Y)NR^6R^7$, $YCR^6R^7R^8$ and $YC(=Y)R^8$; where Y may be NR^8 or O; R^5 is alkyl of

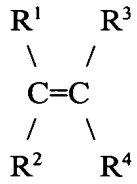
from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^6 and R^7 are independently H or alkyl of from 1 to 20 carbon atoms, or R^6 and R^7 may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and R^8 is H, straight or branched C_1-C_{20} alkyl or aryl; and

R^3 and R^4 are independently selected from the group consisting of H, halogen, C_1-C_6 alkyl and $COOR^9$, where R^9 is H, an alkali metal, or a C_1-C_6 alkyl group; or

R^1 and R^3 may be joined to form a group of the formula $(CH_2)_{n'}$ or a group of the formula C(=O)-Y-C(=O), where n' is from 2 to 6, the group $(CH_2)_{n'}$ may be substituted with from 1 to 2n' halogen atoms or C_1-C_4 alkyl groups, and Y is as defined above; and

at least two of R^1, R^2, R^3 and R^4 are H or halogen.

21. The process of claim 1, wherein at least one of said monomers are of the formula:



wherein at least one of R^1, R^2, R^3 and R^4 are selected from the group consisting of Halogen and $YC(=Y)R^8$; where Y may be NR^8 or O, and R^8 is H, straight or branched C_1-C_{20} alkyl or aryl; and

said process further comprises a second polymerizing step using one or more additional radically (co)polymerizable monomers [conducted prior to said isolating step], conducted in the presence of said transition metal compound and said ligand.--

SUPPORT FOR AMENDMENTS

The claims have been amended to more specifically define the present invention. These amendments are supported by the specification as originally filed. No new matter has been added by these amendments.

REQUEST FOR RECONSIDERATION

Applicant and Applicants' representative would like to thank Examiner Cheng for the courteous and helpful discussion of the issues in the above-identified application on August 21, 1997. The above amendments and following remarks summarize and further expand upon the content of that discussion.

The present invention relates to a process for controlled free radical polymerization, known by the present Applicants as atom (or group) transfer radical polymerization (ATRP). In particular, the present process comprises the steps of radically polymerizing one or more radically copolymerizable monomers in the presence of a system comprising (1) an initiator having one or more radically transferable atoms or groups, (2) a transition metal compound that participates in a reversible redox cycle with the initiator or a dormant polymer chain end, and (3) a ligand meeting certain requirements specified in the claims, such that the transition metal compound and ligand are matched one with the other in order to provide reaction with the initiator to reversibly generate a radical. Under such conditions, the copolymer is formed.

Applicants have found that the present process can provide a radically prepared polymer having highly controlled molecular weight and molecular weight distributions, and

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allows for the production of a wide variety of polymer types, such as block, graph, hyperbranched, gradient, etc. While controlled anionic and controlled cationic processes were known in the art, no one, prior to the present invention, had devised a way to provide such control in a radical system, in order to provide an essentially "living" radical polymerization process. Applicants were the first to do so.

Claims 1-14 and 21-22 stand rejected under 35 U.S.C. §103(a) over Farnham et al or Boettcher et al. Neither of these references can render the present invention obvious. In particular, each of these references is drawn to an anionic polymerization process, not a radical polymerization process as required by the present invention.

Farnham et al disclose a polymerization of acrylic monomers using an initiator that is a tetra-coordinate organotitanium, organozirconium or organohafnium compound. It is particularly important to notice that Farnham et al point out the importance of using aprotic solvents in their process (see col. 6, lines 33-49). This is because of the anionic nature of the polymerizing species. If a protic solvent is used, the protic solvent would terminate the polymerization of Farnham. However, in the present invention, the polymerizing species is a radical. Accordingly, the presence of protic solvents is not a problem. In fact, the present invention is relatively insensitive to solvent type and can even be performed in water or other aqueous solvent mixtures, something that Farnham et al could not dare to do for fear that his polymerization would be terminated or that his initiator would be destroyed.

The scientific community readily understands that Farnham et al is directed to an anionic process, as demonstrated by the attached reference by Haddleton et al. In the very first paragraph on page 3992, Haddleton et al state that although there remains a debate about

the mechanism of the type of group transfer polymerization described by Farnham et al (see ref. 2 from the Haddleton et al paper), "it has been firmly accepted that free radical propagation is not occurring." Accordingly, the reference to Farnham et al cannot render the present invention obvious, since there is no suggestion by Farnham et al that their process is radical based, and it is well accepted in the scientific community that it is not radical in nature.

In fact, in the Haddleton et al reference, there is a comparison of ATRP (the present process, attributed to the present inventors by Haddleton et al at page 3992, paragraph bridging left and right columns) with conventional group transfer polymerization, conventional radical polymerization, and conventional anionic polymerization. As shown in Figure 1 at page 3996, ATRP is completely distinct from conventional Group Transfer Polymerization, as well as from anionic polymerization. As such, based upon the knowledge in the art, the Farnham et al reference cannot render the present invention obvious and the rejection should be withdrawn.

Boettcher et al also discloses conventional group transfer polymerization using an anionic type mechanism. As in Farnham, Boettcher specifically notes that any solvent should be aprotic, characteristic of the anionic nature of the polymerization (see column 7, lines 57-64). Also, Boettcher specifically notes that his initiator species is a source of an anion at column 5. This is obviously a conventional anionic "living" polymerization, not the radical polymerization of the present invention. This is an important distinction, since the ability to polymerize certain monomers depends on the type of polymerization used. By using the present radical based process, it is possible to polymerize a wide range of monomers and

monomer mixtures to prepare a variety of polymer morphologies and is possible to prepare copolymers of monomers that previously could not be copolymerized, since one monomer required anionic polymerization while the other monomer used cationic polymerization.

There is nothing within the Boettcher reference that would suggest the use of the initiator having a radically transferable atom or group and a transition metal compound that participates in a reversible redox cycle with the initator or a dormant polymer chain end in order to reversibly generate radicals onto which further monomer can be added. Prior to the present invention, it was not believed possible to have such fine control of molecular weight and molecular weight distribution in a radical process. Applicants were the first to achieve this. Accordingly, the rejection over Boettcher should also be withdrawn.

Both of the Farnham et al and Boettcher et al references are drawn to polymerization of acrylic type monomers using an anionic polymerization method. Applicants provide herewith a number of literature references that confirm that the polymerization of such monomers using conditions such as described by Farnham and Boettcher result in an anionic polymerization in which the active propagating species is an ester enolate anion. Accordingly, it is well recognized in the art that such polymerizations are not radical polymerization and as such they cannot suggest the present invention.

Applicants submit that the application is now in condition for allowance, and early notification of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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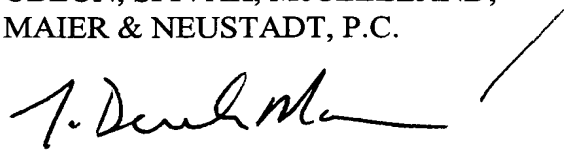

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Macromolecules **1997,** *30,* 3992−3998

Identifying the Nature of the Active Species in the Polymerization of Methacrylates: Inhibition of Methyl Methacrylate Homopolymerizations and Reactivity Ratios for Copolymerization of Methyl Methacrylate/*n*-Butyl Methacrylate in Classical Anionic, Alkyllithium/Trialkylaluminum-Initiated, Group Transfer Polymerization, Atom Transfer Radical Polymerization, Catalytic Chain Transfer, and Classical Free Radical Polymerization

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Received March 5, 1997; Revised Manuscript Received May 5, 1997[⊗]

ABSTRACT: Reactivity ratios have been determined for the monomer pair methyl methacrylate and *n*-butyl methacrylate under a range of polymerization conditions. The value of using reactivity ratios as a mechanistic probe is discussed. Reactivity ratios determined where M1 = MMA and M2 = *n*-BMA are 1.04, 0.81, classical anionic; 1.10, 0.72 , alkyllithium/trialkylaluminum initiated; 1.76, 0.67, group transfer polymerization; 0.98, 1.26, atom transfer radical polymerization; 0.75, 0.98, catalytic chain transfer; and 0.93, 1.22, classical free radical polymerization. The data suggest ATRP and CCTP proceed via radical type propagation. Li/Al-initiated polymerization undergoes an anionic mechanism, while strong evidence is found for an associative, catalyst dependent mechanism for GTP. Galvinoxyl is demonstrated to inhibit GTP as well as free radical polymerization, and it is suggested that neither the use of inhibition nor polymer stereochemistry can be used to distinguish between anionic and radical processes.

Introduction

The mechanism of addition polymerization of methacrylates is often the subject of intense speculation.[1] The ester substituent on the vinyl polymerizable group is an effective electron-withdrawing group activating the bond toward both anionic and radical initiation as well as promoting coordination polymerization. For example, there has been much debate concerning the mechanism of group transfer polymerization (GTP) regarding associative[2−4] or dissociative[5] (anionic) pathways. Indeed, although there remains an active debate concerning the mechanism, it has been firmly accepted that free radical propagation is not occurring. One of the test methods to distinguish between free radical and anionic, or anionic type, polymerizations has been the ability to obtain polymers with narrow molecular mass distributions and controlled number average molecular mass, M_n, so-called living polymerization, as is the case with GTP.[6]

Recently, certain transition metals have been used to promote atom transfer radical polymerization (ATRP).[7−13] ATRP involves abstraction of a halogen atom from a suitable initiating alkyl halide by the transition metal in a reversible reaction that maintains the propagating polymer radical end capped with the halogen, thus greatly reducing the amount of termination. ATRP results in narrow molecular weight distribution polymers, often with polydispersity index, PDI, less than 1.20, with controlled M_n. Thus, "living" polymerization can no longer be considered as a suitable mechanistic test to distinguish between radical and anionic propagation pathways. A suitable mechanistic test for ATRP so as to demonstrate the involvement of homolytic as opposed to heterolytic bond cleavage is not as obvious as it may first seem. Sawamoto uses two tests to demonstrate the involvement of free radicals in the ATRP of MMA as mediated by $Ru_2Cl_2(PPh_3)_3$: (1) the addition of radical inhibitors such as galvinoxyl, **2**, or DPPH immediately stops or prevents polymerization from occurring, and (2) ^{13}C NMR indicates the stereochemistry of the PMMA product to be consistent with a Bernoullian process with stereochemistry similar to PMMA prepared from AIBN in toluene at 60 °C.[7] Matyjaszewski also reports that the stereochemistry of PMMA as prepared from Cu^IX/RX/bipyiridine (X = Cl, Br) is similar to that from classical free radical initiators and that galvinoxyl acts as an efficient inhibitor.[9] Again these two pieces of evidence are used as evidence for a free radical process. Teyssie has demonstrated the use of Ni[{*o*,*o*′-$(CH_2NMe_2)_2C_6H_3$}Br] as being an extremely effective ATRP catalyst; again inhibition by galvinoxyl and a persistence ratio, ρ (where $\rho = 2(m)(r)/(mr)$; m and r refer to meso and racaemic placement of monomer units along the polymer backbone), of close to unity are used as evidence for a free radical mechanism.[12] It is noted that only in this last example are the radicals discussed as *being temporarily confined within the coordination sphere of the metal.*

Group transfer polymerization has been established as proceeding via heterolytic bond cleavage, leading to nucleophilic attack of either a carbon-based anion or a carbon with δ^- charge on the vinyl group of the incoming monomer.[1] The stereochemistry of poly-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S0024-9297(97)00303-2 CCC: $14.00

(methyl methacrylate) from GTP is similar to free radically produced PMMA, with a persistence ratio close to unity. No stereochemical effects have been observed by changing the nature of the SiR_3 protecting group.[14] This is consistent with free radical propagation. As it is firmly established that GTP does not proceed via a free radical process, proposed mechanisms based on stereochemical evidence must be open to question. We were thus interested to examine whether GTP is inhibited by certain free radical inhibitors. The use of *tert*-butyllithium in conjunction with stereochemically hindered aluminum alkyls and phenoxides to mediate the polymerization of methacrylates also proceeds via an undetermined mechanism.[1,15,16] If this mixed metal alkyl system is analogous to immortal polymerization, aluminum porphyrin-initiated polymerization, then the involvement of homolytic bond cleavage has been suggested as a possible step in the polymerization mechanism.[17] Many inhibitors of one type of polymerization may also inhibit others as well, albeit for different reasons. A definitive mechanistic test is required that can be applied to the range of new methacrylate polymerization types.

To date, inhibition and stereochemistry have been the most widely used mechanistic probes for addition polymerization. Free radical inhibitors also invariably interfere with ionic and GTP polymerizations, making their use as mechanistic probes ineffective. Furthermore, the effectiveness of stereochemistry is also questionable as, for example, both GTP and free radical polymerization of methyl methacrylate give very similar polymer microstructures. At the outset of this work, we were interested in investigating if reactivity ratios would clearly distinguish between a range of polymerization processes. Reactivity ratios were considered as a possible mechanistic probe, as they express the effects of at least four rate constants. It is reasonable to assume that the relative changes in the rate constants of propagation and cross propagation for two monomers will not necessarily be exactly the same for different mechanisms. Even when similar monomers such as BMA and MMA are copolymerized, steric, electronic, and relative hydrophobicity will clearly have different effects with either anionic or radical propagation.

Statistical or random copolymerization is important from a scientific viewpoint for examining the reactivities of monomers and propagating centers, and from a technical perspective for the flexibility it offers in polymer synthesis. Reactivity ratios play a central role in the study of copolymerization and are obtained by establishing the relationship between the composition of the monomer feed and the composition of the copolymer produced from that feed. This can be achieved by measuring the concentrations of unreacted monomer (e.g., by GC) or by measuring the composition of the resultant copolymer (e.g., by NMR or IR). Some polymerization mechanisms are specific to monomer types, for example, GTP is extremely effective for methacrylates but inert toward styrene.[18] Catalytic chain transfer polymerization is very effective in reducing the molecular weight of methacrylates but ineffective with acrylates and less active for styrene, than for methacrylates, by 1 order of magnitude.[19,20] If care is used to choose appropriate monomers, which can be copolymerized with similar polymerization behaviours, then a consideration of reactivity ratios might be used as such a mechanistic probe. Reactivity ratios are defined as in eqs 1 and 2, where the symbols have their usual

$$r_1 = k_{11}/k_{12} \tag{1}$$

$$r_2 = k_{22}/k_{21} \tag{2}$$

meanings when applied to copolymerization.[21] These reactivity ratios give a measure of the relative rates of reaction of a polymer radical toward two different monomers. It is expected that if the two monomers have similar reactivities towards a propagating active polymer center, then values should be approximately unity. MMA and BMA provide such a monomer pair, with similar activities with regard to classical anionic polymerization, alkyllithium/trialkylaluminum-initiated polymerization, group transfer polymerization, atom transfer radical polymerization, catalytic chain transfer polymerization, and classical free radical polymerization. This paper describes a study of the reactivity ratios for MMA and *n*-BMA for a range of polymerization types in an attempt to classify new polymerization processes. Monomer 1 is defined as MMA and monomer 2 as *n*-BMA. The effect of certain radical inhibitors on the polymerization of MMA under a range of polymerization types is also discussed.

Measurement of Reactivity Ratios. Experimentally determined average copolymer composition data are related to the composition of the feed through the well-known differential form of the terminal (Mayo–Lewis) model copolymer composition[22,23] equation given by eq 3. The terms F_1 and f_1 represent the mole fraction

$$F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{r_1 f_1^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \tag{3}$$

of monomer 1 in the polymer and monomer feed, respectively. As eq 3 is the differential form of the copolymerization equation, its use is limited to low-conversion copolymerizations (typically <5%), where the symbols have their usual meanings when applied to copolymerization.

A number of assumptions are used in the derivation of eq 3.[22] One of these is the long chain assumption, which states that the monomer incorporated into the chain by initiation, transfer, and termination reactions is negligible compared to the monomer incorporated by propagation. Clearly, this assumption is violated in copolymerizations where short chains are produced, such as those from CCTP. A second assumption is the equal reactivity assumption, which assumes that the relative rates of all the propagation reactions are independent of chain length and depend on the composition of the macroradical only through the terminal unit. Significant violation of these assumptions should show up as trends in the copolymer composition with chain length. This should be examined when reactivity ratios are being determined from relatively short polymer chains.

A number of procedures have been developed for the estimation of r_1 and r_2 based on the Mayo–Lewis model. Most of these procedures have involved the linearization of eq 3 and are statistically unsound.[24] The popularity of these methods has contributed to the large variation in reactivity ratios reported in the literature. It has also resulted in poor estimates of reactivity ratios with misleading confidence intervals. Better estimates are obtained by the use of the error-in-variables-model (EVM) approach. This work used an implementation of the error-in-variables-model approach for estimating reactivity ratios from the differential form of the Mayo–

Lewis equation.[24] The EVM approach is a more satisfactory method of analyzing copolymerization data, since it is statistically sound, allows for the major sources of experimental error to be properly accounted for, has thus been used in the present study.

Recent work has suggested that the EVM approach gives confidence intervals of only approximate shape. One alternate approach is to use nonlinear least squares (NLLS) data evaluation in conjunction with Tidwell–Mortimer criteria.[25] However, NLLS requires some prior knowledge of r_1 and r_2 and narrows confidence intervals quickly through an iterative process. Two experimental compositions are used, corresponding to a high mole fraction and a low mole fraction. In this current work, reliable r_1 and r_2 values were not available in all cases and only one set of experiments was carried out for each type of polymerization. The goal of the current work was to examine the nature of the chain carriers as opposed to determining the definitive set of reactivity ratios.

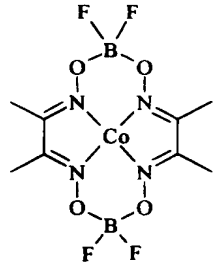
It is noted that we have recently reported the results of a determination of reactivity ratios for MMA and n-BMA by catalytic chain transfer polymerization.[26] The previous study was designed to compare the use of MALDI-TOF and NMR in reactivity ratio determination. The results from the NMR study of CCTP reported previously are included in the present work so as to allow a complete comparison.

Experimental Section

General Information. All reactions were carried out using standard Schlenk line techniques under a nitrogen atmosphere. Methyl methacrylate and *n*-butyl methacrylate were obtained from ICI Acrylics, stabilized with 5 ppm Topanol. Monomers were weighed and mixed prior to being stored under nitrogen over a mixture of 4 Å and 13X molecular sieves and activated basic alumina so as to remove inhibitor, water, and other protic impurities. Triisobutylaluminum (1.0 M solution in toluene) and diphenylethene (Aldrich) were used as received; *tert*-butyllithium (Aldrich) supplied as a 1.7 M solution in pentane and *n*-butyllithium (Aldrich) supplied as a 1.6 M solution in hexanes were stored in glass ampules and titrated against diphenylacetic acid in tetrahydrofuran (THF) before use. Methyl trimethylsilyl dimethylketene acetal (MTS) (Aldrich) was stored over 4 Å molecular sieves in the bottle supplied and used without further purification. Bis(dimethylamino)methylsilane was obtained from Fluorochem Ltd., stored in an ampule under N_2 and used as supplied. Tetrabutylammonium *m*-chlorobenzoate (TBA*m*CB) prepared by the method of Dicker and Sogah[27] was stored in a Schlenk tube under N_2 and prior to being used as a $\sim 8 \times 10^{-3}$ molar stock solution in THF. Tetrabutylammonium acetate (TBAAc) (Aldrich) was dried under vacuum and was stored in a Schlenk tube under an N_2 atmosphere and used as an $\sim 8 \times 10^{-3}$ solution in THF. Ethyl 2-bromoisobutyrate (Aldrich) (98+%) and copper(I)bromide (Aldrich) (99.9+%) were used as received without further purification. 2-Pyridinecabaldehyde *n*-propylimine was prepared as previously reported[13] and stored in a Schlenk tube under N_2 over 3 Å molecular sieves prior to use. Solvents, toluene and THF, were dried over sodium and distilled immediately prior to use. Galvinoxyl (Aldrich) was dried under vacuum and dissolved in THF or toluene as required. AIBN (2,2′ azobis(isobutyronitrile), BDH GPR grade, was used as received.

Three monomer mixtures were prepared with the following [MMA]/[BMA] ratios: 75/25 (563.05 g of MMA, 265.57 g of BMA, [MMA]/[BMA] = 3.011), 50/50 (374.90 g of MMA, 533.89 g of BMA, [MMA]/[BMA] = 0.9973), and 25/75 (188.72 g of MMA, and 799.28 g of BMA. [MMA]/[BMA] = 0.3353).

[Bis[μ-[(2,3-butanedione dioximato)(2−)-O:O′]] tetrafluorodiborato(2−)-N,N′,N″,N‴]cobalt, COBF, **1**, was used as the catalytic chain transfer agent. COBF was prepared according to the procedure of Espenson[28] and was assumed to be the bis(methanol) adduct. COBF was added from a stock solution prepared by dissolving COBF (0.0104 g, 2.32×10^{-5} mol) in toluene (50 mL).



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Polymerizations to Investigate the Effect of Inhibitor. Group Transfer Polymerization. To a 100 mL flask equipped with a nitrogen inlet were added THF (30 mL), MTS (0.057 mL, 2.8×10^{-4} mol), and TBAAc (0.137 mL of a 8×10^{-3} M solution, 2.8×0^{-6} mol) at room temperature. MMA (3 mL, 0.028 mol) was added dropwise to the stirred solution over 90 s. Galvinoxyl (0.401 g, 9.51×10^{-4} mol in 5 mL of THF) was added 45 s after addition of MMA. The reaction was stirred for a further 10 min to allow complete reaction. NMR analysis of the reaction mixture showed polymer and unreacted monomer. SEC analysis of the polymer precipitated from 60−80 petroleum ether, $M_n = 2450$, PDI = 1.91.

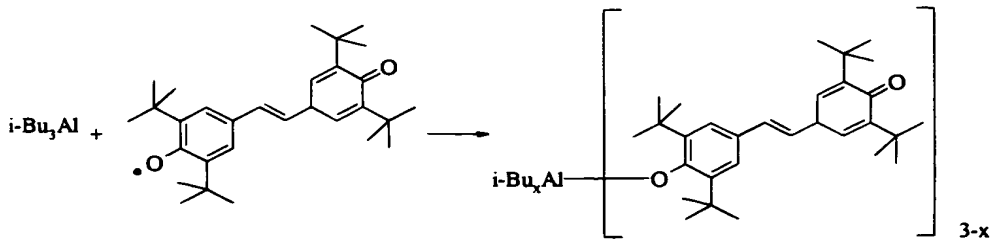
Lithium Alkyl/Aluminum Alkyl-Initiated Polymerization. Toluene (30 mL) followed by *i*-Bu_3Al (1.12 mL of a 1.0 M solution in toluene, 1.12×10^{-3} mol) and *t*-BuLi (0.33 mL of 1.7 M solution in pentane, 5.61×10^{-4} mol) were added to a 100 mL flask equipped with a nitrogen inlet. The flask was subsequently cooled in an ice/salt bath to −5 °C. MMA (3 mL, 0.028 mol) was added rapidly in one continuous addition. Galvinoxyl (0.3318 g, 7.87×10^{-4} mol in 5 mL of toluene) was added 60 s after addition of MMA. The reaction was stirred for a further 15 min. ^{1}H NMR analysis of the reaction mixture showed both poly(methyl methacrylate) and unreacted monomer. SEC analysis of the polymer precipitated from 60−80 petroleum ether, $M_n = 4120$, PDI = 3.71.

Reactivity Ratio Investigation. Group Transfer Polymerization. A 50 mL aliquot of THF was placed in a 250 mL flask equipped with a nitrogen inlet. Then 0.1 mL of bis(dimethylamino)methylsilane, 10 mL of MMA/*n*-BMA (50/50 mixture, 0.078 mol), 0.2 mL of TBA*m*CB of a 8×10^{-3} M solution in THF (1.56×10^{-6} mol), and 0.032 mL of MTS (1.58×10^{-4} mol) were added with stirring at ambient temperature. The reaction was allowed to proceed for 10 min, when it was terminated by the addition of 2 mL of methanol. Diphenylpicrylhydrazyl (DPPH, 0.01 g) was added prior to volatiles being removed from the reaction mixture under vacuum. The polymer product was isolated from the reaction vessel by extraction with a small quantity of dichloromethane and removal of solvent under vacuum at 60 °C until a constant weight was obtained.

Lithium Alkyl/Aluminum Alkyl Initiated Polymerization. In a typical synthesis, a solution of *i*-Bu_3Al in toluene (1.0 mL, 0.001 mol) was added to 100 mL of toluene under an atmosphere of nitrogen and cooled to −10 °C. *t*-BuLi solution (0.29 mL, 4.93×10^{-4} mol) was added to the reaction vessel and stirred for several minutes. The monomer mixture (75/25 MMA/BMA 12.0 mL, 50/50 MMA/BMA 13.3 mL, 25/75 MMA/BMA 14.6 mL) was added quickly in a single addition. Polymerization was terminated after 2 min by the addition of dilute HCl (1.0 mL) and left to stir vigorously for 15 min at room temperature. DPPH was added to the reaction mixture prior to removal of solvent, so as to inhibit further radical polymerization, under vacuum at 60 °C for 2 days.

Classical Anionic Polymerization. 1,1-Diphenylethene (0.74 mL, 4×10^{-3} mol) was dissolved in 20 mL of dry THF freshly distilled from purple sodium/benzophenone under an atmosphere of nitrogen. The solution was titrated by dropwise addition of *n*-butyllithium until a slight red coloration was

Scheme 1



observed; then a stoichiometric quantity of *n*-butyllithium (1.6 mL, 4×10^{-3} mol) was added with stirring over several minutes so as to maintain the reaction temperature below 40 °C. The reaction mixture was then left to stir at room temperature under nitrogen for 24 h. Freshly distilled THF (150 mL) was cooled to −78 °C in a dry ice/acetone bath and titrated under nitrogen with DPHLi until a faint red color persisted. DPHLi (0.63 mL) was added to the reaction vessel followed by addition of the monomer in a single aliquot (75/25 MMA/BMA 12.0 mL, 50/50 MMA/BMA 13.3 mL, 25/75 MMA/BMA 14.6 mL). The reaction was terminated immediately after monomer addition by injection of methanol (1 mL) into the reaction flask. 4-Methoxyphenol (0.2 g) was added to the solution as an inhibitor, and the solvent was removed under vacuum.

Conventional Free Radical Polymerization. In a typical reaction, 10 mL of each MMA/BMA mixture was degassed by three freeze−pump thaw cycles in a Schlenk tube. A 1 mL aliquot of AIBN stock solution (0.0467 g, 0.284 mmol of AIBN in 10 mL of toluene) was added. The solution was frozen, closed under vacuum, thawed to room temperature and heated to 60 °C for 60 min, after which the reaction was quenched by rapid cooling to 0 °C. Duplicate experiments were carried out in each case. The sample was dried to a constant weight *in vacuo*.

Catalytic Chain Transfer Polymerization. A 20 mL aliquot of monomer mixture and 0.03 g of AIBN (1.82×10^{-4} mol) were added to a Schlenk tube. COBF was added as a stock solution in toluene (0.0104 g of **1** (2.32×10^{-5} mol) in 50 mL of toluene). As **1** has a higher C_s for MMA than BMA,[29] more **1** was added as the proportion of *n*-BMA increased. The reaction mixture was heated at 60 °C in a constant temperature water bath for 45 min prior to being quenched by rapidly cooling to 0 °C. The sample was allowed to evaporate overnight and then placed in a vacuum oven at 60 °C until it reached a constant weight (≈3 days).

Atom Transfer Radical Polymerization. A 20 mL aliquot of monomer mixture was placed into a Schlenk tube. Copper(I) bromide (0.1391 g , 9.7×10^{-4} mol) and 2-pyridinecabaldehyde *n*-propylimine (0.4296 g , 2.9×10^{-3} mol) were added with stirring at ambient temperature. Ethyl 2-bromoisobutyrate (0.1898 g , 9.73×10^{-4} mol) was added, and the reactions were then placed in an oil bath (90 °C for 50 min) under N_2 prior to being quenched to 0 °C. After quenching, 1 cm^3 of 50% aqueous hydrochloric acid was added to terminate the reaction. A sample was removed and allowed to evaporate overnight and then placed in a vacuum oven at 60 °C until it reached constant weight (~3 days).

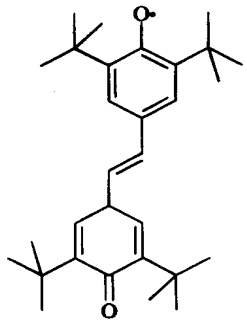
Analysis Methods. SEC was carried out using a Polymer Laboratories (PL) guard column (50 × 7.5 mm), and either one PL Mixed-E column (300 × 7.5 mm), two Mixed-D columns (300 × 7.5 mm), or two Mixed-C columns (300 × 7.5 mm). THF was used as the eluent at a flow rate of 1 mL/min, and data were collected at 1 point/s from a DRI detector. The system was calibrated with log molecular weight expressed as a third-order polynomial of elution volume based on Polymer Laboratories PMMA standards and pure samples of MMA dimer and trimer. No account was taken of the samples being copolymers, and the SEC data are presented as "PMMA equivalent" molecular weights.

Copolymer compositions were ascertained using ^1H NMR in $CDCl_3$ at 250 MHz by integration. These data were used in the EVM program, assuming a 1% uncertainty in the feed and a 5% uncertainty in the copolymer composition.

Results and Discussion

Effect of Galvinoxyl on Group Transfer Polymerization and *tert*-Butyllithium/Triisobutylaluminum-Initiated Polymerization of Methyl Methacrylate. The attempted polymerization of MMA using MTS initiator and TBAAc catalyst in THF at room temperature in the presence of galvinoxyl resulted in no detectable polymerization, reaction A. Addition of galvinoxyl, **2**, to a similar polymerization shortly after initiation, reaction B, results in termination of the reaction and the PMMA has a much broader molecular weight distribution than would have otherwise been expected. Thus galvinoxyl acts as an effective inhibitor for GTP of MMA.

Addition of triisobutylaluminum to a dark solution of **2** in toluene produces a red solution that immediately turns yellow on addition of *tert*-butyllithium. In contrast to the above observations with GTP, this solution



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polymerises methyl methacrylate to give a polymer of reasonably narrow MWD, *C*, and close to the expected M_n, assuming approximately 50% initiator efficiency,[15] M_n(theo) = 10 000 M_n(obs) = 11 600. Addition of **2** shortly after initiation, D, gives a much lower M_n with broader MWD. Addition of galvinoxyl after propagation has been completed, E, again gives a broad MWD polymer that does not reinitiate polymerization on addition of more methyl methacrylate. It appears that if **2** is added at the beginning of the reaction, then it reacts with the metal alkyls to form a new, as yet unassigned, metal-containing species that is active toward polymerization. The new species presumably contains a new aluminum−oxygen bond such as that shown in Scheme 1.

The reaction shown in Scheme 1 is plausible and produces a sterically hindered aluminum phenoxide species that has characteristics similar to those of previously reported aluminum species that are active in methacrylate polymerization.[15,17] Addition of **2** part

Table 1. Experimental Details and Molecular Weight Data for Inhibition with Galvinoxyl Studies

exp	polym type	galvinoxyl ($\times 10^{-4}$ mol)	addition time of galvinoxyl (min)	M_n	PDI
A	GTP	6.16[a]	0		
B	GTP	9.51[c]	2.25	2 450	1.91
C	Li/Al	5.55[a]	0	11 600	1.35
D	Li/Al	5.93[b]	1	4 120	3.71
E	Li/Al	7.87[b]	15	11 480	1.78

[a] Added as a solid at the start of the reaction. [b] Added as a solution in toluene. [c] Added as a solution in thf.

Table 2. Molecular Weight Data and Details of Experiments Carried out To Determine Reactivity Ratios

exp	polym type	composition MMA/BMA	M_n	PDI	% conversion
F	CFR	75/25	487 900	2.07	4.65
G	CFR	75/25	458 700	2.07	6.19
H	CFR	50/50	544 500	1.80	4.69
I	CFR	50/50	535 600	1.75	6.40
J	CFR	25/75	515 800	1.96	7.82
K	CFR	25/75	457 900	2.01	7.83
L	anionic	75/25	12 730	5.65	1.71
M	anionic	50/50	11 790	4.56	2.24
N	anionic	25/75	21 620	3.95	1.71
O	Li/Al	75/25	2 690	6.72	1.25
P	Li/Al	50/50	1 380	3.56	1.83
Q	Li/Al	25/75	2 790	6.96	1.13
R	GTP	75/25			2.41
S	GTP	50/50			2.18
T	GTP	25/75			3.51
U	CCTP	75/25	2 020	2.14	5.29
V	CCTP	50/50	1 610	2.14	4.43
W	CCTP	25/75	2 370	1.87	4.11
X	CCTP	25/75	2 270	1.84	4.17
Y	ATRP	75/25			4.5
Z	ATRP	50/50			5.5
AA	ATRP	25/75			0.88

way through the reaction gives rise to competition between reaction with aluminum alkyl and polymerization termination.

These results demonstrate that **2** can inhibit and terminate polymerizations occurring via an anionic *and/or* anionic type polymerization process. The mode of action of **2** can also be complicated by possible reaction to form new active *or* dormant species. The way in which **2** inhibits either of these types of MMA polymerization is as yet not fully elucidated. However, we may conclude that inhibition by **2** cannot be used as evidence to support a free radical polymerization mechanism.

Reactivity Ratios of MMA and *n*-BMA. The copolymer composition was determined in each case from ^{1}H NMR. The areas from the alkoxy region of the spectrum were used, $\delta(-OCH_3$, MMA) = approximately 3.50−3.65 ppm and $\delta(-OCH_2$, BMA) = approximately 3.80−4.00 ppm. These data were used in the EVM program, assuming a 1% uncertainty in the monomer feed composition and a 5% uncertainty in the copolymer composition. All reactions were carried out to low conversion, Table 2. The resultant point estimates for the reactivity ratios and 95% confidence contours are shown in Table 3 and Figure 1, respectively.

Conventional Free Radical and Anionic Polymerization. The reactivity ratios obtained for conventional free radical polymerization, reactions F−K, of r_1 = 0.93 and r_2 = 1.22 compare very favorably with those reported by Manders using a nonlinear least squares analysis with NMR data with reactions taken to approximately 0.5% conversion.[30] Surprisingly, we have been unable to find literature values for the reactivity

Table 3. Reactivity Ratios from This Work and the Literature

	r_1 (MMA)	r_2 (*n*-BMA)	
CFR	0.93	1.22	this work
CFR	0.91	1.09	ref 30
CFR	0.79	1.27	ref 37
CFR	1.27	1.20	ref 38
ATRP	0.98	1.26	this work
CCTP	0.75	0.98	this work
anionic	1.04	0.81	this work
Li/Al	1.10	0.72	this work
GTP	1.76	0.67	this work
GTP	0.44	0.26	ref 31
GTP	0.52	0.34	ref 31[a]

[a] Data taken from ref 31 reanalyzed using the EVM program.

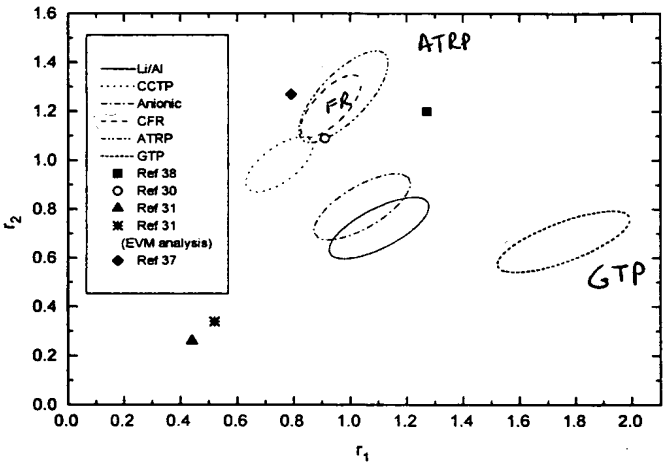


Figure 1. Plot of the reactivity ratio data from this work and literature values.

ratios of MMA and BMA in conventional anionic polymerization in any solvent. Our values, reactions L−N, of r_1 = 1.04 and r_2 = 0.81 indicate that normal anionic polymerization in thf at −78 °C is relatively unselective toward both MMA and BMA, as would be expected. It is useful that the values are significantly different for conventional free radical polymerization and that the 95% confidence intervals do not overlap, Figure 1. This difference in reactivity ratio between classical anionic and free radical polymerization of MMA and BMA allows measuring the reactivity ratio to be used as a probe of the reaction mechanism.

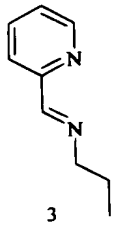
***tert*-Butyllithium/Triisobutylaluminum-Initiated Polymerization.** Reactions were carried out at −10 °C so as to slow the rate of propagation so that less than 10% conversion was reached after 2 min, prior to termination by the addition of acid, reactions O−Q. The molecular weight distributions from these experiments are broader than would be expected in this type of "*living*" polymerization due to the constraints on the experimental procedure from the speed of the reaction. However, this increased MWD is not expected to affect the reactivity ratios appreciably. Both r_1 and r_2 are similar to those for conventional anionic polymerization, 1.10 and 0.72, respectively. The 95% confidence level overlaps with conventional anionic polymerization but not with free radical polymerization, Figure 1. As anionic polymerization is well-known to exhibit strong solvent and temperature effects, this is a striking similarity. Again, this polymerization shows little selectivity between the two monomers and it is concluded that *tert*-butyllithium/triisobutylaluminum initi-

ated-polymerization proceeds via an enol anion in an anionic type polymerization.

Group Transfer Polymerization. The reactivity ratios determined are $r_1 = 1.76$ and $r_2 = 0.67$, reactions R−T. The 95% confidence ellipse does not overlap with values for either anionic or free radical polymerization. This is strong evidence to suggest that GTP is neither radical or anionic. The differences in GTP with anionic polymerization are also good evidence for a coordinative associative mechanism as opposed to a dissociative mechanism, in accordance with Webster.[2] GTP is significantly more selective than either anionic or *tert*-butyllithium/triisobutylaluminum-initiated polymerization. If low concentrations of enol propagating centers are responsible for propagation, a dissociative mechanism, we would expect reactivity ratios similar to those of anionic polymerization. It is also interesting to compare our values with those reported by Jenkins.[31] It is noted that in this previous study polymerizations were taken to 20% conversion using tris(dimethyl)-sulfonium bi-flouride/acetonitrile as catalyst. The data were analyzed using the unreliable Kelen−Tudos methodology.[32] Even when the data are reanalyzed with the EVM program, Table 3, the values determined in the present work are significantly different from those reported by Jenkins. These literature values are also significantly different from those for conventional anionic polymerization. The literature values are consistent with each propagating polymer preferring to cross propagate as opposed to undergoing homopolymerization. Our data show that the rate of reaction of MMA is faster than that of BMA with both propagating poly(methyl methacrylate) and poly(butyl methacrylate). This is what might be expected on the basis of steric considerations. Indeed, the observation by Jenkins that *both* reactivity ratios are less than unity is somewhat surprising. All other studies of GTP reactivity ratios in the literature give two values that are either side of unity. Catalgilgiz reports[33−35] $r_{MMA} = 1.24-1.25$ and $r_{EMA} = 0.30-0.34$ for the GTP of EMA and MMA; these values were calculated using statistically sound linearized semiintegral and nonlinear fully integrated methods.[35] This study supports our observations with the BMA/MMA system. The catalysts used by Jenkins and in the present work are different, Jenkins used bifluoride as opposed to an oxygen-centered TBA*m*CB. The bifluoride is a harder nucleophile and might be expected to promote a more dissociative mechanism; also the formation of trimethylsilyl fluoride from dissociation might be expected to be favored. Clearly, the nature of the catalyst plays an important role in determining the extent of dissociation in GTP. Nevertheless, these two sets of results indicate that the mechanism of GTP under these conditions is not by a purely dissociative mechanism. In addition to this, the mechanism of GTP seems to be dependent upon the exact reaction conditions, especially on the nature of the catalyst used.

Catalytic Chain Transfer Polymerization. As we have previously reported,[26] CCTP gives reactivity ratios that are consistent with a free radical polymerization mechanism. The data are consistent with results reported by Manders,[30] reactions U−X. The mechanism of CCTP is seen to proceed via a free radical mechanism. The relatively poor overlap between conventional free radical and CCTP might be due to the low molecular weight polymers produced by CCTP, which possibly lead to a violation of the long chain assumption used in the analysis.

Atom Transfer Radical Polymerization. ATRP using the Schiff base complex **3** as ligand in conjunction with Cu^{I}Br and ethyl 2-bromoisobutyrate, **4**, give reactivity ratios of $r_1 = 0.98$ and $r_2 = 1.26$, Table 3, reactions



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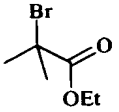

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Y−AA, and Figure 1. The 95% confidence limit completely encompasses that obtained from conventional free radical polymerization, indicating a similar mechanism. Thus, reactivity ratios show ATRP is consistent with a free radical mechanism. It is noted that addition of radical inhibitors to ATRP reactions have been reported to inhibit polymerization. However, work by the current authors has shown that this is not necessarily the case.[36]

General Discussion. The r_1r_2 products for our point estimates for classical radical polymerization and GTP are 1.13 and 1.18, respectively. It is generally believed that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. Recent work aimed at precise estimation of the classical free radical reactivity ratios indicates that for radical copolymerization the product lies within these limits.[30] Similar data are not available for GTP. As alluded to earlier, a value of $r_1r_2 > 1$ may be plausible for steric reasons in GTP. However, the confidence ellipse for GTP does contain a region where $r_1r_2 < 1$. Therefore, the product of the ratios for GTP and classical radical polymerization cannot be distinguished from unity within experimental error. It is worth noting that there are many systems in the literature, even free radical copolymerizations, which contradict the belief that $r_1r_2 = 1$ represents the upper limit for proper copolymerization. For example the table of free radical reactivity ratios in the popular text book Cowie lists reactivity ratios where unity is exceeded for the products of 5 of the 19 monomer pairs listed.[39] Analysis for sequence distribution has not been carried out and thus we cannot comment on copolymer homogeneity, although we have no reason to believe that there is marked inhomogeneity. It is also noted that solvent effects tend to be small or negligible in free radical polymerizations. However, this will not necessarily be the case for nonradical polymerization.

Conclusions

The reactivity ratios for the MMA/BMA monomer pair differ for anionic and free radical polymerization. A measure of these values for new polymerization mechanisms gives an indication of how the propagation in each system proceeds. *tert*-Butyllithium/triisobutylaluminum-initiated polymerization proceeds via a classical anionic mechanism and a stabilized enol anion. GTP differs from this and other reactivity ratios, favoring an associative mechanism. However, the mechanism of GTP does seem to be highly dependent upon the reaction conditions, when literature values for reactivity ratios are considered along with the current data. Both CCTP and ATRP are consistent with a free radical propagation step. Galvinoxyl has been demonstrated to inhibit GTP and also play a role in metal alkyl

initiated anionic polymerization, the mechanism of this inhibition is as yet undetermined. As such the effects of radical inhibitors on a polymerization cannot be used as a definitive mechanistic test. This coupled with the stereochemistry of poly(methacrylates) being similar in GTP and conventional free radical polymerization results in a new more reliable indication of the polymerization mechanism being required. Reactivity ratios have been demonstrated to give such an indication. The use of a reliable statistical interpretation of suitably resolved ^{1}H NMR spectra is an excellent mechanistic probe. It is apparent that the differences in polymerization mechanism highlighted by reactivity ratios were anticipated, as discussed earlier. This approach is, however, limited to polymerization processes with an appropriate monomer set.

Acknowledgment. We would like to thank the EPSRC (K.G.S., ROPA:GR/K35952; M.C.C., GR/33538; C.W., ROPA:GR/K65652) and ICI (C.T.) for funding. We would also like to thank Andrew Shooter and Dr. Stuart Richards for invaluable discussions and ICI Acrylics for monomers.

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Makromol. Chem., Macromol. Symp. **67**, 373-386 (1993)

TERMINATION PROCESSES IN GROUP TRANSFER POLYMERIZATION

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Abstract: Two major termination processes in the GTP of methacrylates and acrylates have been studied. For methacrylates, intramolecular cyclization is the dominant, if not sole, termination reaction. Both cyclization and O/C-silyl isomerization of the chain end are observed for acrylates. Oligomerization experiments were used to study the relative rates of cyclization and propagation and the influence of temperature, catalyst and dp. Under typical GTP conditions for methacrylates, cyclization is at least two orders of magnitude slower than monomer addition.

INTRODUCTION

Group transfer polymerization (GTP) is a silicon-mediated process for the preparation of methacrylate and acrylate polymers at room temperature (Ref. 1). The process involves the Michael reaction of a silyl ketene acetal end group with the monomer in the presence of a Lewis acid or anionic catalyst. GTP displays characteristics of a living polymerization including relatively narrow dispersities, control of MW by initiator/monomer stoichiometry and the ability to synthesize block and functional polymers. It can be argued that GTP is not a living polymerization in the strictest definition because both termination (Ref. 2) and chain transfer (Ref. 3) have been reported. Chain termination can become an especially serious problem when the goal is to prepare block copolymers or functional polymers. The aim of the present work was to characterize more fully termination reactions in the GTP of methacrylates and acrylates. It is important to define conditions which minimize the contributions of termination and chain transfer to the overall polymerization.

Schemes 1-3 outline three major termination processes in GTP. The

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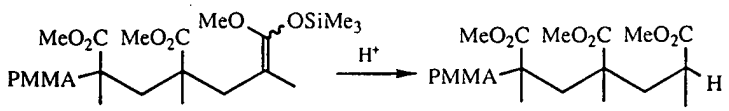
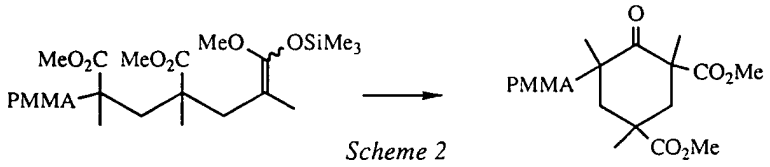
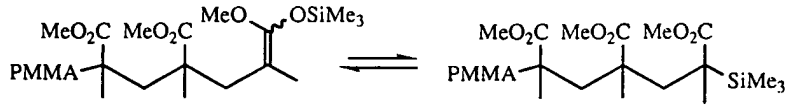


Scheme 1



Scheme 2

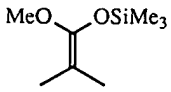


Scheme 3

presence of impurities from solvent and monomer can lead to premature termination by quenching the active center (Scheme 1). Side-reactions between silyl ketene acetal initiators and bifluoride catalysts have been reported (Ref. 4). These side-reactions can lead to the same type of termination product (proton quenching) as in Scheme 1 although the full extent of their contribution to GTP has not been fully defined. Cyclization of the chain end to form an inactive cyclohexanone end group (Scheme 2) is the major mode of termination in the GTP of methacrylates (Ref. 2). A third termination process is a silyl ketene acetals isomerization (Scheme 3) in which the trimethylsilyl group migrates from the oxygen to the α-carbon of the chain end (Ref. 5). This O/C silyl isomerization is a termination process because C-silyl compounds are not effective initiators of GTP (Ref. 1). In this article, results for cyclization and O/C silyl isomerization in the GTP of acrylates and methacrylates are presented.

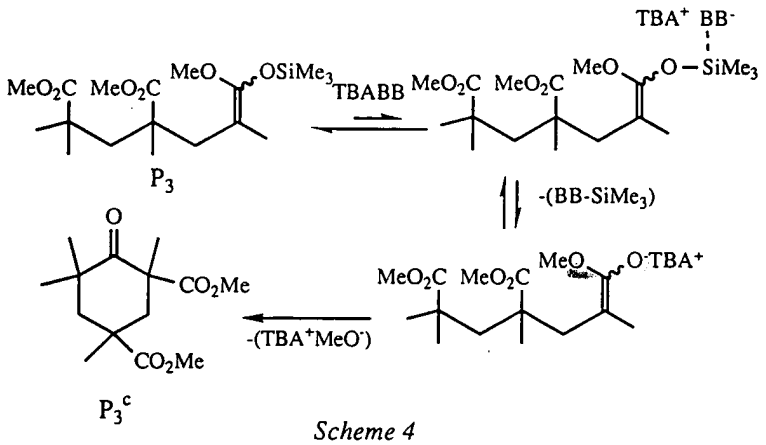
CYCLIZATION IN THE GTP OF METHACRYLATES

The cyclization shown in Scheme 2 is an intramolecular nucleophilic attack by the silyl ketene acetal end group on the backbone ester. The propensity of a GTP oligomer to self-terminate is demonstrated by the 85% isolated yield of 2,4-(dicarbomethoxy)-2,4,6,6-tetramethylcyclohexanone (P_3^c) from the overnight reaction of 0.050 mol of methyl methacrylate (MMA) and 0.025 mol [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, P_1, in THF using 0.00125 mol of tetrabutylammonium bibenzoate (TBABB) as cat-



P_1

alyst. This process is analogous to the major termination pathway in anionic polymerization of methacrylates, commonly referred to as back-biting (Ref. 6,7). The occurrence of cyclization in GTP argues for the involvement of ester enolate intermediates which are the active centers in anionic polymeri-



Scheme 4

zation. Scheme 4 depicts a proposed mechanism where the first step is catalyst complexation to form a pentacoordinated siliconate. The siliconate then may dissociate to form an enolate paired with the counterion of the anionic catalyst; cyclization of the enolate leads to the terminated chain end. There is accumulating experimental evidence consistent with ester enolates intermediates (Ref. 8-10).

Kinetics of Cyclization

The kinetics of cyclization have been studied for GTP oligomers prepared from MMA. Rates are based on the following model:

$$\text{cat} + P_i \overset{K^*}{\rightleftharpoons} P_i^* \xrightarrow{k_i^c} P_i^c$$

If it is assumed that the catalyst complex, P_i^*, achieves a steady state concentration, and that the rate of catalyst complexation is fast relative the rate of cyclization (k_i^c), then the rate of reaction is given by:

$$\frac{-d[P_i]}{dt} = \frac{k_i^c K^* [P_i] [cat]_o}{1 + K^* [P_i]} \qquad (1)$$

The integrated form of this equation depends on the magnitude of equilibrium constant (K*). Müller and co-workers (Ref. 11) have shown that K* >>1 for bifluoride catalysis while K* <<1 for oxyanions (bibenzoate, benzoate). This conclusion was made based on the kinetic rate order with respect to initiator concentration for MMA addition. Therefore, there are two limiting cases for the integrated form of equation 1. Thus, the disappearance

- $K^* [P_i] >> 1$; bifluoride, this leads to
$$[P_i] = [P_i]_o - k_i^c [cat]_o t \qquad (2)$$
- $K^* [P_i] << 1$; oxyanions, this leads to
$$\ln ([P_i]/[P_i]_o) = k_i^c K^* [cat]_o t \qquad (3)$$

of living ends by cyclization follows pseudo zero-order kinetics for bifluoride. Bifluoride is strongly bound to the silicon so that the concentration of the catalyst complex remains constant during the process. When "$[P_i]_o$-$[P_i]$" is plotted versus "t", a straight line is obtained (Figure 1) for at least the first half-life of a bifluoride-catalyzed cyclization. Plotting the bifluoride data in a first-order manner does not give a straight line. The deviation from linearity at higher conversion probably reflects a breakdown in the assumptions used to derived equation (2). In many experiments, straight lines were obtained for conversion up to four half-lives. In all cases, rates are based on the initial slope; multiple kinetics runs compared very well. The slope of the line gives the apparent rate constant (k_{app}) which is related to the real rate constant by : $k_i^c = k_{app}/[cat]_o$.

In contrast, the rate of living end disappearance in the presence of oxyanion catalysts follows first order kinetics (see Figure 2) in accord with equation (3). The slope of an oxyanion rate plot gives an apparent rate constant which is related to the product of the complexation equilibrium constant and the rate constant by : $k_{app}/[cat]_o = k_i^c K^*$.

FT-IR spectroscopy is a useful tool for studying the termination of MMA oligomers (Ref. 2). The silyl ketene acetal functionality of the living oligomers has a $\nu_{C=C}$ stretching absorption at 1687 cm^{-1} and a backbone ester $\nu_{C=O}$ absorption at 1740 cm^{-1}. The cyclohexanone termination product has a characteristic ring $\nu_{C=O}$ absorption at 1716 cm^{-1} (for P_3^c, ε = 608).

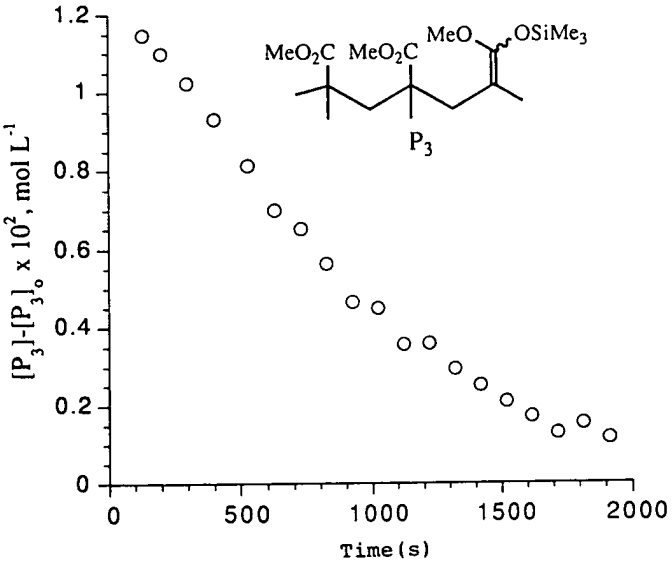


Figure 1. Zero-order time-conversion plot for cyclization of P_3; THF, 25°C, $[P_3]_o = 0.0125$ M, $[TPSHF_2]_o = 2.5 \times 10^{-5}$ M.

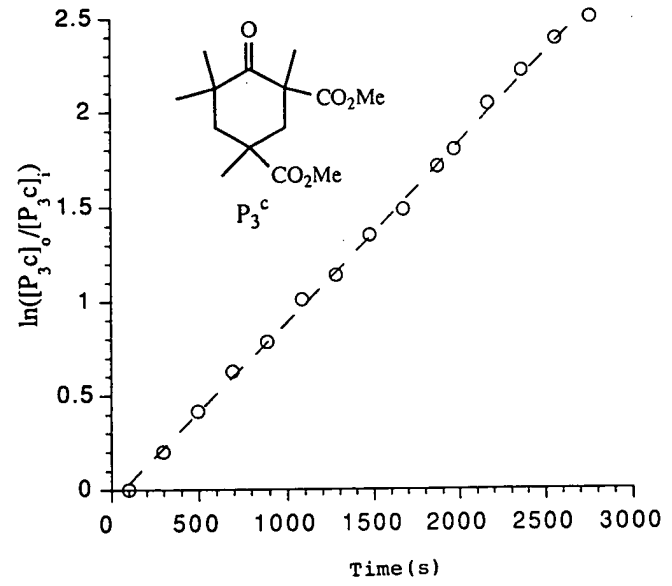


Figure 2. First-order time-conversion plot for cyclization of P_3; THF, 25°C, $[P_3]_o = 0.25$ M, $[TBABB]_o = 0.0125$ M.

Infared spectroscopy was used to characterize changes in oligomer solutions prepared from different starting ratios of MMA : P_1. The oligomerization of P_1 and MMA was performed in THF at room temperature with TBABB or tris(piperidino)sulfonium bifluoride ($TPSHF_2$) catalysis. In addition to studying oligomer mixtures, the discrete cyclization reaction of P_3 was also examined . This approach relies on the independent synthesis of P_3 which has been previously described (Ref. 12). A stopped-flow apparatus was used to mix solutions of catalyst and P_3. Kinetic information on GTP termination was typically obtained by following the decrease in the silyl ketene acetal peak because it had the least overlap with adjacent peaks. For the FT-IR study of oligomer mixtures, the monomer and initiator P_1 were either mixed using the stopped-flow apparatus or the solutions were transferred from reactions performed in glassware. Following monomer consumption (typically 2-3 min), the loss of living ends was monitored by the disappearance of the living end absorption at 1687 cm^{-1}.

Table 1 contains rates obtained from linear regression of concentration

Table 1. Termination Kinetics of Group Transfer Oligomers Based on FT-IR Spectroscopy[a]

Exp. No.	Reaction Conditions	Rate of Cyclic Ketone Formation,[b] L mol^{-1} s^{-1}	Rate of Living End Loss,[c] L mol^{-1} s^{-1}
1	0.25 M P_3 0.0125 M TBABB		0.062
2	0.0125 M P_3 2.5 x 10^{-5} M $TPSHF_2$		2.9[d]
3	2:1 MMA:P_1 0.0125 M TBABB[e]	0.008	0.011
4	3:1 MMA:P_1 0.0125 M TBABB[e]	0.009	0.010
5	5:1 MMA:P_1 0.0053 M TBABB[f]		0.0018
6	5:1 MMA:P_1 0.001 M $TPSHF_2$[f]		0.61[d]

[a] THF, 25°C, rate = $k_{app}/[cat]_o$; for TBABB, rate = k_i^c K*; for $TPSHF_2$, rate = k_i^c. [b] Based on the growth of the $\nu_{C=O}$ at 1716 cm^{-1}. [c] Based on decrease of $\nu_{C=O}$ at 1687 cm^{-1}. [d] sec^{-1}. [e] 0.25 M P_1. [f] 0.1 M P_1.

time profiles using the appropriate integrated rate equation. There are several important points to be drawn from Table 1. The rates of cyclic ketone formation and living end loss are very similar for the 2:1 and 3:1 oligomer mixtures which indicates that cyclization is the major termination pathway for MMA oligomers. This fact is supported by product analysis using GC and GPC where only cyclic oligomers are observed after 24 hours (Ref. 2). The second fact worth noting is that the rate of cyclization for linear trimer P_3 is several times higher than the rate of cyclization for the oligomer mixtures (compare experiments 3 and 4 with experiment 1 and also compare experiments 2 and 6 and in Table 1). Rates of cyclization for the oligomer mixtures reflects the summed average rate for the cyclization of all oligomers present, which in the case of the 3:1 mixture includes oligomers up to dp=12 (based on GPC). Therefore, the rate of cyclization for P_3 must be greater than the rates of cyclization for the higher oligomers. The third fact revealed by Table 1 is that cyclization is much faster for bifluoride catalysis relative to bibenzoate.

Temperature Dependence of Cyclization

The temperature dependence of cyclization for GTP oligomers generated by mixing 5:1, MMA:P_1 was determined. Table 2 shows the rates of cyclization at four different temperatures and Figure 3 shows the corresponding Arrhenius plot. From the slope and intercept, the activation parameters for cyclization can be determined. They are given in Table 3 along with the activation parameters determined by Mai and Müller (Ref. 13) for GTP propagation catalyzed by tris(dimethylamino)sulfonium bifluoride ($TASHF_2$).

Table 2. Rate of Cyclization for GTP Oligomers Prepared from 5:1 MMA:P_1[a]

Temperature, °C	Rate, s^{-1} [b]
25	0.61 ± .06
35	0.9 ± .1
45	1.5 ± .1
55	2.1 ± .1

[a] $[P_1]_o$ = 0.2 M, $[TPSHF_2]_o$ = 0.0005 M, THF. [b] Rate = $k_{app}/[cat]_o$, values are average of at least four determinations.

Müller (Ref. 14) found that as the size of the counterion increases, the activation parameters for MMA addition in anionic polymerization more closely resemble GTP values. Unfortunately, the activation parameters for cyclization in anionic polymerization have not been determined so it is difficult to make conclusions about the mechanism of GTP cyclization.

Table 3. Comparison of Rate Constants and Activation Parameters for Propagation and Cyclization with Bifluoride Catalysis

	propagation[a]	cyclization[b]
E_a, kJ mol^{-1}	16.9	34.3
log A	6.8	5.8
Rate (-40°C)	1250 L mol^{-1} s^{-1}	0.013 s^{-1} *c*
Rate (25°C)	6900 L mol^{-1} s^{-1} *c*	1.6 s^{-1}

[a] $[MMA]_o$ = 0.18 M, $[P_1]_o$ = 0.001 M, $[TASHF_2]_o = 6 \times 10^{-5}$ M (Ref. 13). [b] $[MMA]_o$ = 1.0 M, $[P_1]_o$ = 0.2 M, $[TPSHF_2]_o$ = 0.0005 M.
[c] Extrapolated value.

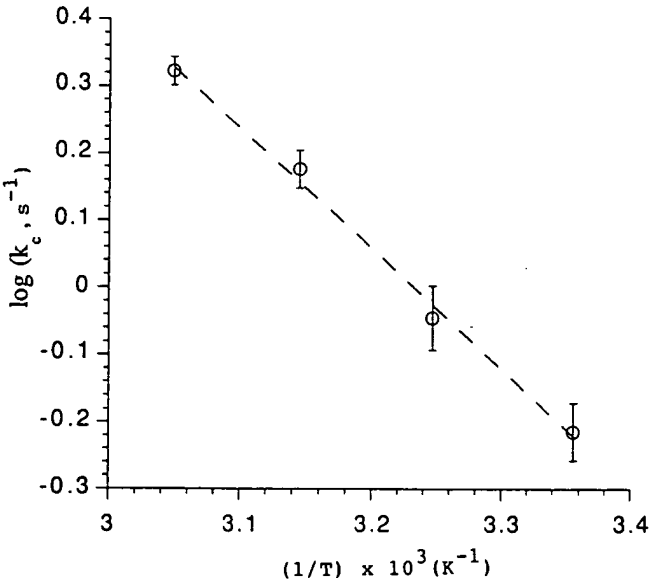
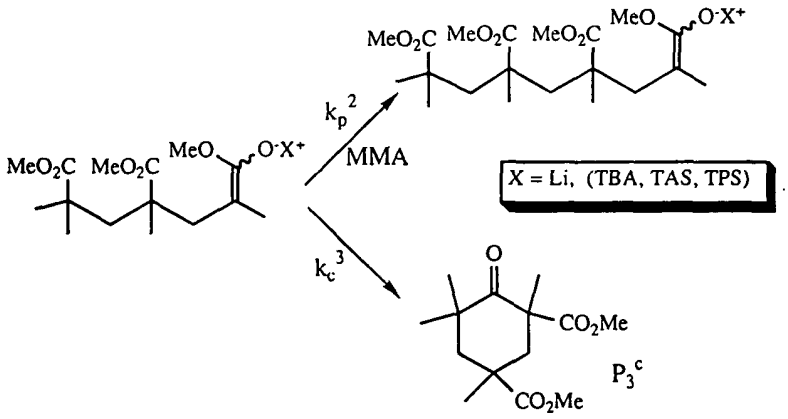


Figure 3. Arrhenius plot for the cyclization of GTP oligomers prepared from 5:1 MMA:P_1.

It is possible to compare the rate ratio of propagation to cyclization for oligomers of MMA. Müller, Lochmann and Trekoval (Ref. 6) studied the oligomerization of MMA using the lithium ester enolate of methyl isobutyrate (MIB-Li) as an initiator. From a study of product distribution versus time, they were able to obtain rate constants for MMA addition (k_p^2) and cyclization (k_c^3) of P_3 (see Scheme 5). Table 4 contains the rate ratio (k_p^2/k_c^3) for GTP with TBABB catalysis. The discrete rate constant for the

addition of MMA to P_3 was determined using stopped-flow FT-IR spectroscopy (Ref. 12). The ratio of propagation to cyclization depends on the concentration of MMA because the overall reaction order is different for the two processes. As the monomer concentration decreases, so does the rate ratio. At sufficiently low MMA concentration, cyclization actually becomes faster than propagation. Inspection of Table 4 reveals that GTP has a much



Scheme 5

Table 4. Comparison of Silicon and Lithium Mediated Oligomerization of MMA at 25°C in THF

End group	k_p^2/k_c^3, L mol^{-1}
lithium ester enolate[a]	8
silyl ketene acetal[b]	250[c]

[a] $[MMA]_0$ = 0.1 M, $[MIB\text{-}Li]_0$ = 0.05 M (Ref. 6). [b] $[MMA]_0$ = 0.125 M, $[P3]_0$ = 0.25 M, $[TBABB]_0$ = 0.0125 M. [c] k_p^2 from Ref. 12.

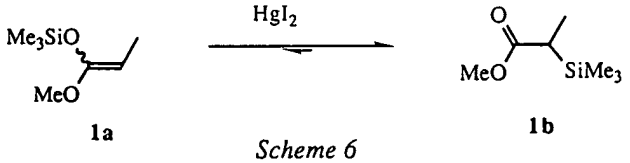
lower propensity to terminate relative to lithium-mediated polymerization. A better comparison would be GTP versus anionic polymerization using a larger counterion. Müller (Ref. 14) has observed that the rate of cyclization decreases as the size of the counterion increases so the difference observed in Table 4 may simply reflect the difference between a tetrabutylammonium and lithium counterion assuming that the active species in both polymerizations is an ester enolate. The GTP rate ratio in Table 4 represents a lower limit because the cyclization of P_3 is faster than the higher oligomers (Ref. 2) while the propagation rate constant remains constant regardless of

oligomer dp (Ref. 12). This is supported by the propagation/cyclization rate ratio of 4300 at room temperature for bifluoride catalysis (see Table 3).

TERMINATION IN THE GTP OF ACRYLATES

O/C Silyl Isomerization

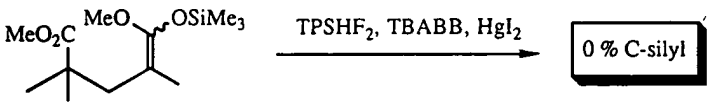
Silyl ketene acetals can undergo E/Z stereoisomerization and O/C silyl isomerization (Ref. 5,15). Silyl ketene acetals derived from acetate esters prefer the C-silyl isomer (Ref. 16). For silyl ketene acetals derived from propanonate esters, the position of the O/C silyl equilibrium depends on the degree of substitution at the α-carbon (Ref. 5). Silyl ketene acetal **1a** is often used as an initiator for acrylate polymerization (Ref. 4). Exposure of this initiator to 0.4 mole % HgI_2 in $CDCl_3$ for 6 days results in complete conversion to the C-silyl form (**1b**). Larger alkyl substituents on the ester



1a **1b**

Scheme 6

reduce the amount of C-silyl isomer at equilibrium. For isobutyrates, the O-silyl form is preferred. Exposure of the 1:1 adduct (P_2) of MMA and P_1 to several different catalysts resulted in no formation of the C-silyl isomer (Scheme 7). Silyl ketene acetal P_2 is a good model for the propagating end in the GTP of methacrylates. Therefore, the lack of O/C silyl isomerization



P_2

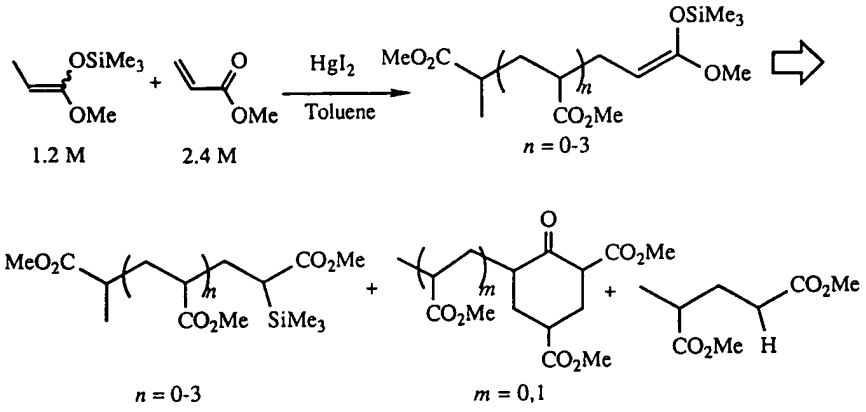
Scheme 7

indicates that this is not an important termination process in the methacrylates. Sogah, et al. (Ref. 1) observed 25% C-silyl formation for the isobutyrate initiator P_1 in the presence of tetrabutylammonium *m*-chlorobenzoate. However, we did not observe any isomerization of P_1 in the presence of HgI_2 (Ref. 5).

Oligomerization of Methyl Acrylate

Oligomerization studies were performed to explore the nature of termination reactions in the GTP of acrylates. Experimental methods and instrumentation are identical to those described in earlier work (Ref. 2,5,12). Mercuric

iodide (HgI_2) was used as the catalyst for the acrylate polymerization because on previous work which indicated that this catalyst gave improved control (Ref. 17). Two different monomer addition experiments were performed. A 2:1 ratio of methyl acrylate (MA) to initiator **1a** (1.2 M) were allowed to react in toluene with 1 mole % HgI_2 (Scheme 8). Monomer was added in a batch mode in one experiment during which the temperature rose to 106°C. In the second experiment, MA was added slowly so that the temperature remained at 25°C. After 6 hr, the catalyst was removed by filtration and the volatiles removed in vacuo. The ^1H NMR spectrum contained $SiMe_3$ resonances at 0 ppm, which is consistent with C-silyl isomers. Additionally, the



Scheme 8

^{13}C NMR also did not contain resonances characteristic of the O-silyl chain end. The ^{29}Si NMR spectrum contained resonances at 6.699 and 7.003 ppm characteristic of C-silyl groups. ^{29}Si NMR is a powerful diagnostic tool for studies of GTP reaction products. Table 5 contains the chemical shifts of some silicon compounds relevant to GTP. Examination of Table 5 reveals that ^{29}Si NMR can easily distinguish between O- and C-silyl groups, E and Z stereoisomers of silyl ketene acetals and typical products from the side-reactions of silyl ketene acetals with acetonitrile (Ref. 18,19) and catalyst (Ref. 4) (Me_3SiF, $C_6H_5CO_2SiMe_3$). In addition to revealing the absence of O-silyl species in the product mixture, ^{29}Si NMR also indicates that the C-silyl group is attached to the chain end of the oligomers and is not internal (C-silyl groups which would result from a chain transfer process). Chain transfer involving the backbone hydrogen of an acrylate oligomer would lead to a

C-silyl group with the same chemical shift environment as an isobutyrate which should appear near 9.90 ppm. This is not observed. Prior to detailed

Table 5. 54.6 MHz 29Si NMR Chemical Shifts; THF-d_8 (unless otherwise noted), shifts are relative to TMS.

Silicon Compound	^{29}Si Chemical Shift (solvent)
1a	20.085 (E), 20.391 (Z)[a]
P_1	18.33
P	18.992 (Z), 20.732 (E),
P_3	18.912 (Z), 20.732 (E)
Methyl 2-trimethylsilylisobutyrate	9.90
1b	6.976[b]
Me_3SiF	33.25
Me_3Si-O-$SiMe_3$	7.16
Me_3Si-CH_2CN	4.21
$C_6H_5CO_2$-$SiMe_3$	24.919

[a] $CDCl_3$. [b] C_6D_6.

GC-MS analysis, samples from the batch and feed monomer experiments were stored for several weeks. Table 6 contains a summary of the product analysis where sample storage time prior to GC-MS analysis is indicated. The relative amounts of each compound are based on GC analysis and are not corrected for detector sensitivity. Cyclization products akin to those observed in the GTP of MMA were found in the product mixtures.

For the monomer feed oligomerization experiment, both cyclics and C-silyl oligomers up to tetramer were observed in addition to some H-dimer (see Scheme 8). The batch monomer oligomerization experiment, corresponding to a high reaction temperature (106°C) afforded mainly C-silyl oligomers (n = 0,1,2 in Scheme 8). Reanalysis after allowing the product mixture to stand for 8 additional weeks revealed partial conversion of the C-silyl oligomers to cyclic trimer and tetramer (m = 0,1 in Scheme 8). Despite the removal of HgI_2 by filtration, the oligomeric products probably still contained traces of the catalyst which presumably would continue to catalyze product changes.

The acrylate oligomerizations have demonstrated that both O/C-silyl isomerization and cyclization are important termination processes in the HgI_2 catalyzed GTP of MA. C-silyl formation is dominant at higher reaction tem-

peratures. The C-silyl oligomers are capable of conversion to cyclic oligomers, although the mechanism of this transformation is not clear.

Table 6. GC-MS Results for Methyl Acrylate Termination Experiments

Product[a]	Feed MA Addition	Batch MA Addition	
Sample Storage[b]	2 Weeks	2 Weeks	10 Weeks
H-Dimer	16	19	15
α-Silyl Dimer (n=0)	22	28	17
Cyclic Trimer (m=0)	19	2	41
α-Silyl Trimer (n=1)	23	51	5
Cyclic Tetramer (m=1)	10	[c]	11
α-Silyl Tetramer (n=2)	10	[c]	11

[a] Both reaction mixtures contained traces (< 5%) of higher oligomers; see Scheme 8 for structures. [b] Period of time between reaction workup and GC-MS analysis. [c] Not determined.

CONCLUSIONS

Two termination processes in GTP have been characterized: intramolecular cyclization (back-biting) and O/C-silyl isomerization. Both of these termination reactions are slower than monomer addition but become more important as the concentration of monomer becomes low. Cyclization is the major termination pathway for methacrylates. The rate of cyclization is highest for the 2:1 adduct (P_3) of MMA and initiator P_1 under anionic catalysis. For catalysis by bifluoride, a comparison of propagation and cyclization reveals that the rate of monomer addition is at three orders of magnitude higher that the rate of cyclization. Acrylate oligomers formed by HgI_2 catalyzed GTP self-terminate by both O/C-silyl isomerization and cyclization. Preliminary results suggest that higher reaction temperatures favor O/C-silyl isomerization.

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Attachment

Makromol. Chem., Macromol. Symp. **67**, 365-371 (1993)

MECHANISM OF GTP: CAN ALL OF THE AVAILABLE DATA BE ACCOMMODATED?

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ABSTRACT: Group transfer polymerization (GTP)[a] of acrylic monomers is a living system mediated by a trialkylsilyl capped growing chain end. The fact that it operates at temperatures as high as 100° C differentiates GTP from living anionic polymerization, which at best operates at 25° C for hindered methacrylates. To accommodate all of the mechanistic data available it appears that at least two mechanistic pathways are required: an associative process for mild nucleophilic catalysts and a dissociative process for strong nucleophilic catalysts.

INTRODUCTION

GTP, the first method for controlled polymerization of methacrylates that operates at above room temperature, was reported nine years ago (Ref. 1). Although it is not a perfect living system, (chain termination occurs at about 1/100th the rate of chain propagation), GTP is finding continued use for polymethacrylate synthesis. Living anionic polymerization of methacrylates gives polymer architecture control similar to GTP but low synthesis temperatures must be used. Recent work by Teyssié, however, has shown that some relief from the low temperatures can be obtained by adding Lewis acids to the system (Ref. 2). In work exhibiting a striking similarity to GTP, Yasuda has isolated the eight-membered ring intermediate **1** from reaction of 2 equivalents of MMA with $[(C_5Me_5)_2SmH]_2$. This intermediate is an exceptionally efficient initiator for living polymerization of MMA (Ref. 3). A similar intermediate or transition state has been postulated for GTP (Ref. 4). Although conditions for living polymerization have not been worked out, the polymerization of MMA by Cp_2ZrMe_2 under

[a] See Glossary at end of paper

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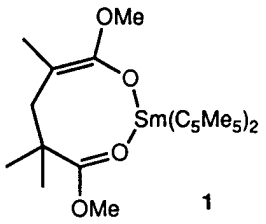
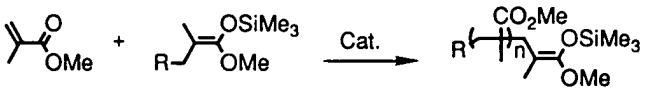
Cp_2ZrMe^+ catalysis recently reported by Collins (Ref. 5) appears to be operating by a mechanism similar to Lewis acid catalyzed GTP (Ref. 6).



1

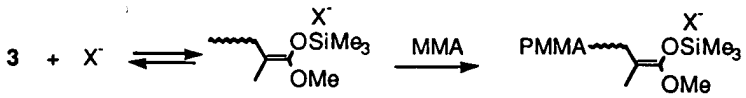
GTP MECHANISM

The overall process for GTP is shown in equation (1) for polymerization of MMA. In anion-catalyzed GTP, the acrylic monomer adds to the silyl ketene acetal-ended polymer, 3, either by covalent insertion (equation 2) or through generation of a small amount of ester enolate-ended polymer in equilibrium with silyl-ended chains (equation 3). To accommodate all of the data available, a dual pathway is required where the path followed depends on (a) the nature of the catalyst, (b) the temperature, (c) the pressure, and (d) the type of monomer. The associative pathway (2) is favored by weakly nucleophilic catalysts, Lewis acid catalysts, high pressures and low temperatures. Strongly nucleophilic catalysts and reactive monomers favor pathway (3).



monomer initiator living polymer (1)

2 3



(2)

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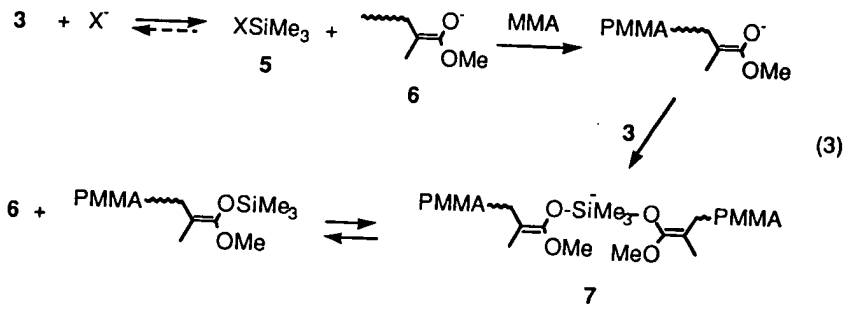
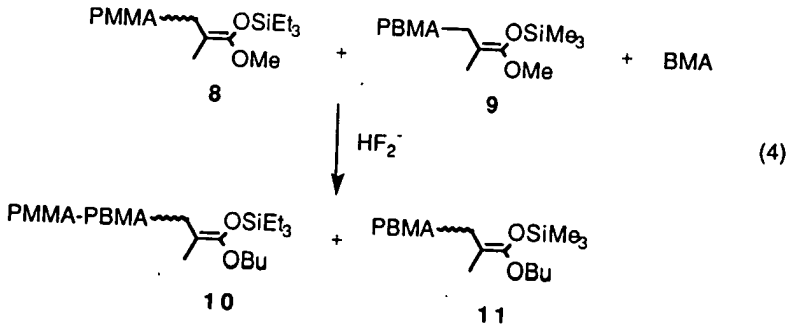


(3)

NATURE OF CATALYST

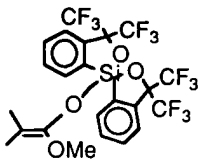
Pathway (2) requires that each trialkylsilyl group remain with the chain it started with. Pathway (3) requires complete exchange of silyl end groups since the enolate, **6**, is recapped by a trialkylsilyl from the entire pool of polymer chains. Double-labeling experiments to differentiate between the associative and dissociative mechanism are complicated by the fact that trialkylsilyl end groups exchange in the presence of catalyst even when no monomer is present (Ref. 7). Fortunately, at the oligomer stage, this rate of exchange is slower than the rate of polymerization. Thus when one adds butyl methacrylate to a mixture of **8** (m.w. ~3000) and **9** (m.w. ~3000) in the presence of TAS HF_2 catalyst at room temperature and quenches the polymerization in 2 to 3 minutes, one obtains **10** (m.w. ~4000) insoluble in hexane and **11** (m.w. ~4000) soluble in hexane. Nmr analysis shows that very little, if any, exchange of silyl end groups has occurred and confirms that **10** is a block polymer. In a like manner no exchange was observed when the label groups were switched.



(4)

Similar double-label experiments by Quirk (Ref. 8) that used high and low molecular weight PMMA to enable separation gave product exhibiting substantial exchange. However, the time frame for these experiments was considerably longer (20 minutes) than that used by Sogah and Farnham. Bywater and Martin caution that the more hindered triethylsilyl-ended polymer may be adding monomer much more slowly than the trimethylsilyl-ended polymer and thus exchange would be minimal (Ref. 9).

If **5** is a fluorosilane, it does not exchange with silyl groups on the active chain ends. However, if **5** is a trialkylsilyl ester, it exchanges rapidly with silyl chain ends (Ref. 10) and lowers the rate of polymerization (Ref. 11). This retarding effect could be the result of a shift in the equilibrium which produces **6** or due to complexation of catalyst with **5**, thus lowering the catalyst concentration. Polymers formed in the presence of excess trialkylsilyl esters have lower molecular weight dispersities and their molecular weights correspond more closely to theory than those synthesized without the additive (Ref. 11).



12

The fact that **12** initiates polymerization of MMA at room temperature supports the associative mechanism (Ref. 4), since **12** is a covalent analog of the activated initiator, **4**. However, since anionic polymerization of MMA at room temperature proceeds to completion in the presence of excess **2** (R=H) but stops at 14% conversion in the absence of **2** (R=H), the dissociative mechanism is operating in this case (Ref. 12). Polymer in the molecular weight range of 5000 was made. Since the ratio of **2** (R=H) to monomer determines the M_n of the polymer, the exchange of end groups must be faster than the rate of polymerization. One wonders if this would be true for formation of polymer in the 50,000 M_n range, where the molecular handshake, **7**, necessary for exchange would be slowed by the bulk of the polymer molecules.

Another complicating factor is that the catalyst reacts destructively with the initiator especially when no monomer is present (Ref. 9). Although no mechanism studies have been conducted, it is almost certain that Lewis acid catalyzed GTP is an associative process operating by activation of the monomer (Ref. 6).

TEMPERATURE

In a double-label experiment, similar to that conducted with bifluoride, Sogah and Farnham found that dimethylphenylsilyl groups exchanged with dimethyltolylsilyl groups at -70° C but not at -95° C under catalysis by TAS Me_3SiF_2 (Ref. 4). One can therefore assume that an anionic mechanism with exchange is operating at -70° C, while an associative mechanism is operating at -90° C. It is interesting to note that with tetrabutyl ammonium as the gegenion, dissociative GTP proceeds at room temperature (Ref. 12) whereas with TAS Me_3SiF_2 as catalyst at room temperature, no polymer forms. Moreover, since GTP works well at room temperature with TAS HF_2, its role cannot be to simply generate ester enolate from the silyl ketene acetal end groups.

PRESSURE

Under ~3000 atm pressure, no catalyst is needed for GTP to operate. Under these conditions there is little doubt polymerization is occurring by an associative mechanism (Ref. 13). Molecular weight control was poor. No polymer was obtained in control experiments without the silyl ketene acetal initiator.

TYPE OF MONOMER

A dissociative process has been proposed for GTP of very reactive monomers especially those that would require 10- and 12-membered rings for associative transfer, e.g., pentadienoates and heptatrienoates (Ref. 14).

CONCLUSIONS

Regardless of the mechanism, GTP has proven to be a useful method for controlled synthesis of acrylic polymers. The almost identical properties of polymers prepared by GTP and anionic polymerization

points to an anionic, i.e., dissociative mechanism. GTP can be forced to operate by an anionic mechanism by using an anionic catalyst that is nucleophilic enough to initiate polymerization itself if no GTP initiator is present. However exchange studies with bifluoride at room temperature or with $Me_3SiF_2^-$ at -95° C show that the silicon on the reactive polymer end remains associated with the same polymer chain it started with during propagation. To accommodate both results a dual mechanistic pathway is required, one where weak nucleophiles, such as bifluoride, activate the silyl group but do not cleave it and where strong nucleophiles remove the silyl group to generate small amounts of enolate ends which add monomer and exchange rapidly with the silyl ketene acetal ends. Additional studies with different catalysts and at low temperatures are needed to clarify the situation.

Wrong book at preceding Quirk's paper

GLOSSARY

BMA	Butyl methacrylate
Cp	Cyclopentadienyl
GTP	Group transfer polymerization
MMA	Methyl methacrylate
OAc^-	Acetate
PBA	Poly(butyl acrylate)
PBMA	Poly(butyl methacrylate)
PMMA	Poly(methyl methacrylate)
TAS	Trisdimethylaminosulfonium

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GROUP TRANSFER POLYMERIZATION - A CRITICAL OVERVIEW

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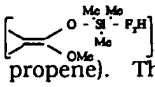
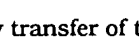
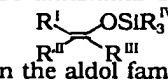
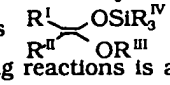
ABSTRACT: Available evidence on the mechanism of group transfer polymerization is presented. The data are discussed in terms of the possibility that the chain carriers are enolate anions rather than the originally suggested pentacoordinate silicon complexes.

Group transfer polymerization (GTP) is a relatively recently developed technique for initiating a 'living' polymerization of vinyl monomers having electron withdrawing groups, principally acrylates and methacrylates (1-5). Monomers such as styrene and dienes cannot be polymerized. Developed in the research laboratories of duPont, it belongs to a newer group of such polymerization mechanisms which require an initiator and also a catalyst. In this respect it has similarities with recently described living cationic systems (6).

The initiators most commonly used are silyl ketene acetals although C-trialkylsilyl compounds (e.g. Me_3SiCN or Me_3SiCR_2COOMe) which may generate silyl ketene acetals by addition to methacrylates or by rearrangement can be used, although less effectively. Tin and germanium analogues (e.g. Me_3CSnR_2COOMe) of the C-silyl type can also be used (3). The catalysts, used in much smaller amounts than the initiator, may be anions such as fluoride, bifluoride, trimethyldifluorosiliconate, azide, cyanide and salts of carboxylates and phenolates. The associated cations used are large and diffuse such as tetraalkylammonium (R_4N^+), tris (dialkylamino) sulphonium (TAS^+) or tripiperidino sulphonium (TPS^+). In addition Lewis acid catalysis has been used principally for acrylate polymerization (3) where the normal basic catalysts lead to termination reactions. Compounds such as $ZnCl_2$, HgI_2, R_2AlCl have been used with solvents such as chlorinated hydrocarbons or toluene.

 CCC 0258-0322/93/$ 04.00

In GTP catalyzed by anions the solvent used is normally tetrahydrofuran. Acetonitrile has been used in a few cases (1,7,8) but it is not totally inert. The mechanism of polymerization is suggested to be (1,2) catalyst interaction with the silicon atom of the initiator to form a pentacoordinate anionic intermediate  e.g. from MTS (1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene). This is active in the addition of monomer probably via a cyclic transition state to form a dimer having the same  end group as the initiator, by transfer of the trialkylsilyl group to the carbonyl group of the monomer. Hence the term group transfer polymerization. The process repeats with dimer, trimer etc. Only catalyst activated chain ends, a small fraction of the total, will grow but since the system is 'living' and with a final D.P. equal to $\frac{[M]_o}{[I]_o}$ (the monomer to initiator ratio) and with a narrow molecular weight distribution, a rapid interchange of activated and dormant chain ends must occur. This is achieved by catalyst "hopping" between chain ends.

To polymer chemists this system may be unfamiliar but in synthetic organic chemistry the use of enol silyl ethers  , silyl ketene acetals  as enolate equivalents in the aldol family of C-C bond forming reactions is a well established technique (9). Particularly they are used as substitutes to lessen side-reactions produced by the more reactive enolate ions themselves in additions to aldehydes and ketones. Anionic polymerization is essentially a repeated Michael condensation (the addition of enolate anions to αβ unsaturated carbonyl compounds). The list of GTP catalysts described above is to a large extent common to a list of acid and base catalysts for aldol condensations using silicon based intermediates. For example fluoride ion source catalysis of the addition of enol silyl ethers to aldehydes (10) or trimethyl silyl ketene acetals to αβ unsaturated ketones (11). In both these two studies $TAS^+ F_2SiMe_3^-$ was used as catalyst which probably dissociates at least partially to F^- and Me_3SiF. Noyori in fact, showed that benzylmethylketone enolate ion was formed near quantitatively from a 1:1 mixture of its enol silyl ether and the catalyst on removal of tetrahydrofuran and the volatile Me_3SiF (10). The isolated enolate failed to react to any measurable extent with benzaldehyde, unless excess Me_3SiF or enol silyl ether was added. This does not mean that enolate anions are not important intermediates in the normal condensation procedure. It results from the fact that the bond forming reaction:

$$R^{I}-\overset{O^{-}TAS^{+}}{\overset{|}{C}}=CH-R^{II}+RCHO \rightleftharpoons R^{I}-\overset{O}{\overset{\|}{C}}-CHR^{II}-\overset{O^{-}TAS^{+}}{\overset{|}{C}}HR \quad (1)$$

does not favour the product anion (formation of a less stable alkoxide anion from a charge delocalized one). Trapping of this anion to regenerate the catalyst is a requirement of catalyzed aldol condensations, (12) which therefore only proceed in presence of the intermediates such as Me_3SiF normally present. The duPont research group differentiate between O-SiR_3 bond cleavage with catalysts such as $Me_3SiF_2^-$ and addition (coordination) to the silicon of silyl ketene acetals by the preferred catalyst HF_2^- (3). The former anion is also a good GTP catalyst (1) but of course this may be due to dissociation to F^- and Me_3SiF.

Recent work on the products isolatable from larger than catalytic amounts of HF_2^- anion with MTS show that the product is methyl isobutyrate and Me_3SiF (13) and under some conditions this proceeds further to give the condensation product methyl 2,2,4-trimethyl-3-oxopentanoate (P_1^c) (14) described by Lochmann as the condensation product of methyl lithioisobutyrate with methylisobutyrate (15). This shows that cleavage of the O-$SiMe_3$ bond of MTS can occur even with HF_2^-. Indeed although the hydrogen bond strength in HF_2^- is unusually strong, O-$SiMe_3$ cleavage may well be an exothermic process due to the extremely high Si-F bond strength in the Me_3SiF formed.

The use of bifluoride catalysis preferentially is conditioned at least in part by the extreme difficulty (perhaps impossibility) of drying fluoride salts. This leads to difficulty in handling and the moisture present is deleterious to the polymerization process. This is less likely for oxyanion catalysis of GTP, nevertheless "bibenzoate" or "biacetate" salts rather than simple benzoate or acetate salts seem to be required for optimum results (16). The hydrogen bonding is very much weaker than in the bifluoride anion, so that the dissociation process

$$(RCOO)_2H^-M^+ \rightleftharpoons RCOO^-M^+ + RCOOH \quad (2)$$

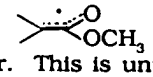
is certain to occur. The active centres are still considered to be of the pentacoordinate type eg $\left[\text{ketene-O-Si(Me)(Me)(OMe)-O-C(=O)-R}\right]^-$ for simple acid salt catalysis. This raises the problem why bianions give better results in a system which is obviously sensitive to potential proton sources as shown by the need for rigorous exclusion of water (1,3). The explanation given, is that they serve to

maintain a low concentration of mono-oxyanions via the above equilibrium. Indeed better results are observed at lower concentrations of mono-oxyanion when used alone, but the reason for this is obscure. It is recognized that the free acid liberated will give an equivalent amount of methylisobutyrate from attack on the initiator, but little initiator will be lost under normal experimental conditions due to the low catalyst/initiator ratio used. The other product, the trimethylsilyl ester of the carboxylic acid must have some catalytic activity since addition of extra amounts of such trimethylsilylesters is recommended to enhance the 'livingness' of polymerizations. (16,17)

Chain ends may also be attacked by the free acid to produce "dead" polymer rather than methylisobutyrate together with again trimethylsilyl ester, but in this case carboxylate anion is also regenerated. Generally more complexities are admitted in this type of catalysis, but in reality potentially the same problems due to splitting of the hydrogen bond in the bifluoride case to give free acid cannot be excluded either as we have seen earlier. It is also not clear whether both the bi-oxyanion and the oxyanion freed by the dissociation process 2 are regarded as activators for adding monomer, or what the relative contributions to the process are. If the bianion is quite effective, then the argument above, suggesting the purpose of using bianions is to release small amounts of mono anion, is difficult to understand.

Much less data is available on Lewis Acid catalyzed GTP systems.(3,18) Zinc halide catalysis requires 4-5 times as much metal halide as initiator and as much as 20% with respect to the monomer, so it is hardly a realistic catalyst. Aluminum based systems can be used at more reasonable ratios but are restricted to low temperature polymerizations. HgI_2 seems to be the most efficient catalyst, usable at room temperature in amounts less than 10% of the initiator.(19) Acid (protonic or Lewis) promotion of simple aldol type condensations is a well documented process, often leading to less side products than conventional anion catalysis.(20) With metal halides the reactions are not catalytic requiring for example 1:1:1 amounts of silicon compound, unsaturated ketone and $TiCl_4$, the latter being the most common catalyst, although $SnCl_4$ and BF_3: Etherate are also used. The mechanism is apparently not well understood (21). Mechanisms suggested include the formation of an enolate (The reaction of $TiCl_4$ for example with MTS is known to produce ),(22) coordination of $TiCl_4$ with both silyl compound

and carbonyl compound in a cyclic transition state or even simple activation of the carbonyl compound by Lewis acid coordination(23). In the polymerization of acrylate monomers it is reported that titanium ester enolates alone will initiate the reaction in absence of catalyst (24) so an enolate route for polymerization is at least plausible.

The reaction products obtained by mixing MTS with various metal halides have also been reported. $TiCl_4$ is unique in the production of dimethyl tetramethylsuccinate, most probably via the intermediacy of the above titanium^{IV} enolate and Me_3SiCl. This enolate can decompose to give $TiCl_3$ and an enolate radical  (25) which dimerizes to the tetramethyl-succinic acid ester. This is unusual, however, the main product normally being the compound P_1^c (Claisen product) (26) exactly as found for enolate ion reactions. This is the case for Zn and Al halides, $FeCl_3$ alone gives a mixture of both products. The reactions seem to be slow, however, and in presence of monomer, for example, these products could be suppressed except at low monomer concentrations.

More recently mercuric iodide has been reported as being a most efficient catalyst requiring only small amounts to be effective in the condensation of silyl ketene acetals with aldehydes and ketones, as well as being the most efficient catalyst for GTP of acrylates. The mechanism suggested involves (19) the coordination of HgI_2 dimer (fig. 1) to MTS activating it towards monomer

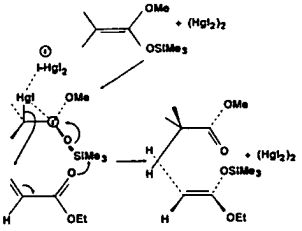
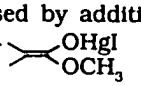


Fig. 1. Mechanism of GTP of acrylates with HgI_2 as catalyst

addition. A similar coordination would activate the silylketene acetal chain ends. The HgI_2 dimer complex would have to be dissociated and recomplexed rapidly as with HF_2^- catalysis. This suggestion is somewhat different to classical GTP in that the catalyst is postulated to complex to the double bond rather than to the silicon atom. A more detailed study of this system (27) has found a slow polymerization process showing an induction period, which can be suppressed by addition of $(CH_3)_3SiI$. The first step is suggested to be formation of  (or its C-substituted isomer) from HgI_2 + MTS. The

two then interact to give $(CH_3)_3Si^+HgI_3^-$, whose anion acts as the activator of the initiator or polymer silyl ketene acetal end groups. This alternative mechanism resembles more the base catalyzed system.

Many of the more detailed mechanistic studies on GTP involve methylmethacrylate as monomer, MTS as initiator and particularly bifluoride ion as catalyst in carefully dried tetrahydrofuran. If carried out at room temperature with a low monomer to initiator ratio, the cyclic trimer of methyl methacrylate, dimethyl 1,3,5,5-tetramethyl-6-oxo-1,3-cyclohexane dicarboxylate (P_3^c) described by Lochmann et al. in the reaction of methyl α-lithioisobutyrate with methyl methacrylate was found (28). Similar cyclic trimers had been also found in the reaction of phenyl magnesium bromide and diphenyl magnesium with methyl methacrylate (29). Below -20°, this is not an important product if the reaction is terminated within a reasonable time at operating temperature with methanol.(13) Correspondingly as the monomer/initiator is increased, the amount of cyclic trimer decreases. Cyclization of longer chain ends is possible but much less likely if anionic polymerization is a guide.

Some kinetic studies on the variation of polymerization or initiation rate with catalyst and initiator concentration have been made, but regrettably agreement between different laboratories is not good. This is true for both reaction order and rate constant, although comparisons are often made difficult by the large concentration differences of the reactants used. The most detailed studies have been made by the Mainz group, so that these will be examined primarily. (30,31) Their observed rates for bifluoride catalysis appear to be higher than reported by Bandermann under reasonably similar conditions (14) or to the initiation rates reported by Brittain.(32) In the latter case the reaction orders are however, quite different.

The duPont mechanism can be simplified if chain initiation is rapid as is equilibration, and with the usual assumption of k_p independent of chain length to (30):

$$C + P_i \underset{}{\overset{K^*}{\rightleftharpoons}} P_i^* \qquad (3)$$

$$P_i^* + M \xrightarrow{k_p} P^*_{i+1}$$

where C is the catalyst, P_i the inactive chain and P_i^* the activated chain. Under these conditions, the first order constant for monomer consumption, is given by the formula:

$$\left(-\frac{1}{[M]}\frac{d[M]}{dt}\right) = k_{app} = k_p\left(\frac{K^*[I]_o}{1 + K[I]_o}\right)[C]_o \qquad (4)$$

Rearranging we find, $\frac{1}{k_pK^*} + \frac{[I]_o}{k_p} = \frac{[C]_o[I]_o}{k_{app}}$ (4a)

On plotting $\frac{[C]_o[I]_o}{k_{app}}$ vs $[I]_o$ we should obtain a straight line of intercept $1/k_pK^*$ and slope $1/k_p$. Alternatively $\frac{[C]_o[I]_o}{k_{app}}$ should be independent of $[C]_o$. The results from the Mainz group are shown in fig.2. Only the points at low $[I]_o$

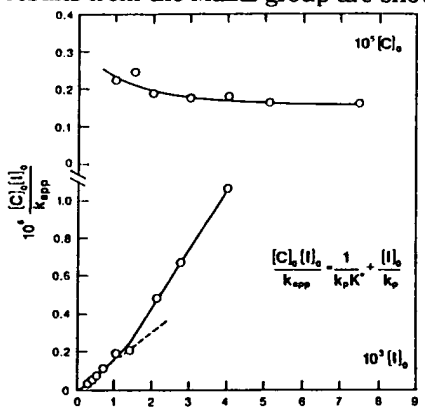


Fig. 2. Plot according to Eq. (4a) for estimation of k_p and K^*

are consistent with the equation giving an essentially zero intercept, indicating $K^* > 1.6 \times 10^4\ M^{-1}$ and $k_p \sim 6700\ M^{-1}s^{-1}$. The points at higher initiator concentration appear also to be on a straight line but this gives an impossible negative intercept. They correspond to the polymerizations in which a noticeable induction period was observed, possibly due to slow initiation, where k_{app} was obtained from the maximum rate. Their too low rates could be due to underestimation of the slope of the logarithmic plots and/or catalyst destruction since they correspond to $[C]_o/[I]_o < 1.5 \times 10^{-2}$. The upper part of fig. 2 shows that at constant $[I]_o$ and variable $[C]_o$ the argument tends to the expected constant value at higher $[C]_o$ values indicating the same failure as in the plot of variable initiator. It is also of interest that Bandermann's results at $[C]_o/[I]_o \sim 1\text{-}2 \times 10^{-3}$ give much lower k_{app} and that Brittain's initiation rate constants were obtained at $[C]_o/[I]_o$ values in the range $1\text{-}8 \times 10^{-4}$ largely because of a very high $[I]_o$ (0.25 M).

Over a restricted range of $[C]_o$, the Mainz group's result do fit the supposed mechanism, but it is a disappointingly small range. It should be recognized that because of low solubility of the $TAS^+\ HF_2^-$ catalyst in THF,

concentrations were in the 10^{-5} M region. Catalyst destruction at the lower end of the range might be a problem, so perhaps a study using $TPS^+ HF_2^-$ which is more soluble might be of interest.

Some data are available from the Mainz group on catalysis by bibenzoate (33,34) which produces much slower polymerization rates, but the study shows an even greater incidence of induction periods, together with incomplete conversions. This indicates termination is more important in this type of catalysis. Bearing these problems in mind, with both tetrabutylammonium and tris(dialkylamino)sulfonium cations, k_{app} was found to be close to first order in initiator concentration which suggests that unlike bifluoride ion catalysis the activation equilibrium is well over to the left, i.e. most of the catalyst is uncomplexed. For $K^* \leq 1$ the rate should be proportional to the product $[I]_o \times [C]_o$. Details have, so far, not been reported on the catalyst order but simply that it can be between -0.3 and +1 according to the type of oxyanion and reaction conditions. A negative exponent is not simply explainable, but fractional orders in both $[I]_o$ and $[C]_o$ would be expected for intermediate values of the activation equilibrium constant.

Disregarding the uncertainties which are evident, a fit at any point with the above equation would be consistent with any mechanism involving an equilibrium between active and dormant chain ends. This would be true for equilibration between enolate anion and silylated chain ends. With fluoride-based systems a rapid cleavage of silyl groups might be expected so that the rate would be expected to be proportional to catalyst concentration and independent of initiator concentration. What would happen in the case of mono-oxyanion polymerization is less sure but a slow cleavage of silylated end groups is possible. Bianion catalysis could cause more rapid cleavage induced by the carboxylic acid as noted above. This could conceivably lead to more complex kinetic behaviour.

These considerations raise the problem of how to distinguish between a pentacoordinate silicon anion activator and a classical enolate anion as reactive agent. The similarity of side products between GTP and classical anionic systems has been noted above in terms of P_1^C and P_3^C formation as well as the lesser suitability of acrylates in both systems. To this can be added the similarity of polymer microstructure and its temperature variation between GTP and what would be expected from an anionic system which used a large

counter-ion of the size of TAS^+(33) for example. An anionic system operating at room temperature is not as unlikely as at first thought, as shown by Quirk's recent work on initiation of methyl methacrylate polymerization by the tetrabutylammonium salt of 9-methylfluorene at room temperature.(35) A polymer with $\bar{M}_w/\bar{M}_n$ = 2 was formed, indeed which terminated at 14% conversion. Addition of MTS to such a system however produced 100% conversion and polymer with $\bar{M}_w/\bar{M}_n$ = 1·2 with $\bar{M}_n$ close to that calculated from the monomer to MTS ratio. This means that the enolate anion pair chain ends can rapidly exchange with ketene silyl acetal ended chains formed in the system. This system in fact parallels the alkoxide/excess parent alcohol system used by Gee in the polymerization of ethylene oxide in dioxane.(36) He showed this would lead in the case of rapid exchange of $-ONa^+$ and -OH chain ends to narrow molecular weight distribution polymer with a $\overline{DP}_n$ of $[M]_o/[ROH]_o$ if alcohol was in large excess. A similar system involving alkoxide initiated polymerization of methyl methacrylate itself, in presence of excess alcohol has been briefly described (37) which will give polyalkyl-methacrylates of $\bar{M}_w/\bar{M}_n < 1.2$ and molecular weights determined by the monomer to alcohol ratio. There is thus ample evidence of workable anionic systems proceeding at room temperatures.

Indeed enolate anions as reactive intermediates in GTP were considered by the original authors (2,4) but were rejected on the basis of experiments designed to determine whether exchange would occur on the polymerization time scale between two preformed polymers having different silyl alkyl or silyl aryl end groups in presence of catalyst, or between one of these polymers and trimethylsilyl fluoride. The latter experiment was designed on the basis that resilylation of enolate anions by TMSF might be required for exchange as is necessary in classical aldol condensations. This is not likely as seen from the above experiments on room temperature anionic polymerizations. The former exchange experiment ("double exchange"), is the key experiment because it should show if the enolate anion - silylacetal exchange, the more likely exchange mechanism, is operating. No exchange was in fact observed with bifluoride catalysis, (1,2) which appears to rule-out an anionic mechanism. Some potential problems with the experiments have been, however, pointed out, which will not be discussed here. Reference should be made to the original description of the experiment (2,38) and to the comments on them.

(6,13) The choice between a pentacoordinate silicon intermediate and a simple enolate ion (pair) is vitally dependent on the "double exchange" experiments. The results recently reported by Quirk (39) using a slightly diferent technique are extremely important in this context, as they show that considerable exchange can occur within a 20 minute period. While some reports (eg. 34) show complete polymerization in a much shorter time when all monomer was added at once, polymers with a wide distribution of molecular weight were formed, particularly at low conversion. Slow addition of monomer to the system is known to produce the narrowest molecular weight distributions so that Quirk's results would be more relevant to such conditions. On the other hand, as noted above, other authors report considerably lower polymerization rates in any case.

An anionic mechanism for base catalyzed GTP of methylmethacrylate has gained credence by these later exchange experiments. Besides explaining the similarities noted above between GTP and conventional anionic systems, such a mechanism would also give the simplest explanation for the Bernoullian chain statistics observed in the microstructure of polymethylmethacrylates prepared by GTP (40). With a counter-ion such as TAS^+ or TPS^+ where the charge is shielded by large organic groups, it could be expected that an enolate ion would be nearly all in the trans configuration as observed in anionic polymerizations using K^+[222] as counter ion (90% trans) (41). The structure of the silyl ketene acetal ended dimer is, in contrast, mixed (~70% trans), (42) which probably would be true of longer chains. Such a mixture of structures, which are known to interconvert only slowly is expected (40) to give polymers with more complex chain statistics.

Acceptance of an anionic mechanism would make a knowledge of the rate of formation of anions in GTP systems of some interest. The only evidence available at present is due to Bandermann (14) who reported that at $[I]_o$ = 10^{-2}M and with $[HF_2^-]_o$ between 10^{-3}M and 10^{-2}M, catalyst/initiator reaction is complete in 5 min. at room temperature. This raises the possibility that under some experimental conditions, particularly with $[C]_o < 10^{-5}$M, slow formation of initiating anions is another possible cause of induction periods. Unfortunately, the lack of agreement on the reference polymerization rates makes comparisons with this and other rates rather difficult.

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Attachment

Makromol. Chem., Macromol. Symp. **67**, 351-363 (1993)

MECHANISTIC ASPECTS OF GROUP TRANSFER POLYMERIZATION

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Abstract: The experimental evidence supporting the involvement of enolate anions in group transfer polymerization(GTP) is reviewed. The results of silyl group exchange studies between living silyl ketene acetal-ended oligomers under typical GTP conditions are discussed. It is concluded that the observations of significant amounts of silyl group exchange in the presence of polymerizing monomer are not consistent with the originally proposed "associative mechanism" based on the GTP Criterion which precludes intermolecular silyl group exchange.

INTRODUCTION

Group transfer polymerization (GTP) provides a unique methodology for the synthesis of acrylate and methacrylate polymers with well-defined structures and low degrees of compositional heterogeneity (Refs. 1-5). The polymerization is initiated by silyl ketene acetals in the presence of nucleophilic or electrophilic (Lewis acid) catalysts. In contrast to living anionic polymerizations of acrylates and methacrylates which generally must be carried out at low temperatures (e.g., -78°C) (Refs. 6,7), group transfer polymerization exhibits the characteristics of a living polymerization at room temperature and above. The scope and limitiations of GTP for the synthesis of polyacrylates and polymethacrylates have been investigated extensively (Refs. 1-5). Especially for alkyl methacrylates, polymers can be prepared with control of a wide range of compositional and structural variables including molecular weight, molecular weight distribution, copolymer composition and microstructure, branching and chain-end functionality (Refs. 1-5).

In contrast to the well-defined aspects of the synthetic utility of GTP, the mechanism of GTP remains a subject of controversy (Refs. 8,9). In the initial publications of the inventors of GTP at DuPont, this process was mechanistically described as "group transfer polymerization" based on the postulate that each

CCC 0258-0322/93/$ 04.00

chain-growth step for the nucleophile-catalyzed polymerization explicitly involves transfer of a trialkylsilyl group from the silyl ketene acetal chain end of a growing polymer to the carbonyl group of the incoming monomer to form a new silyl ketene acetal chain end via a hypervalent silicon intermediate and a rather unusual 8-membered ring transition state as shown in Scheme 1 (Refs.10-13). This mechanism has generally been accepted with little modification or criticism, except to postulate a non-concerted, stepwise process in which carbon-carbon bond formation precedes the oxygen-oxygen silyl group transfer (Refs. 14-19).

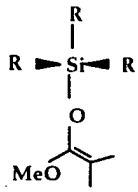
A considerable body of experimental evidence is now available which is consistent with an alternate mechanistic hypothesis that ester enolate anions are the propagating intermediates in group transfer polymerization of alkyl methacrylates:

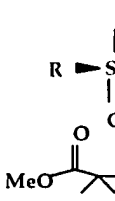
1. Although GTP exhibits the characteristics of a living polymerization, a termination reaction is observed which involves a chain-end cyclization reaction to form a cyclohexanone-type chain end (Ref. 20); this process is analogous to the termination product of ester enolate anions in corresponding anionic polymerizations (Ref. 21).

2. Chain transfer is observed to carbon acids which have pK_a values in the range of 18-25 for methyl methacrylate GTP (Ref. 22). Estimates of the pK_a of the conjugate acids of ester enolate anions range from 24.5 (Ref. 23) to 27-28 (Ref. 24) in aqueous solution to 30-31 in dimethyl sulfoxide (Ref. 24). This chain transfer process is analogous to the tetrabutylammonium fluoride catalyzed silylation of aldehydes and ketones with ethyl (trimethylsilyl)acetate for which an ester enolate anion intermediate has been postulated (Ref. 25).

3. The stereochemistry of GTP for methyl methacrylate is not unique to GTP as originally claimed (refs. 12,15); it is essentially the same as that observed for anionic polymerization when the counterions compared are the same (Ref. 9) or similar (Ref. 18). Thus, the stereochemistry of the polymer obtained with either the caesium or tetrabutylammonium cations as counterions from the silicon-mediated process (GTP) is essentially the same as that observed for the polymer obtained from the corresponding anionic polymerization in the absence of silyl ketene acetal as shown in Tab.1

Schem





Tab. 1. Compa
THF by GTP

Pro
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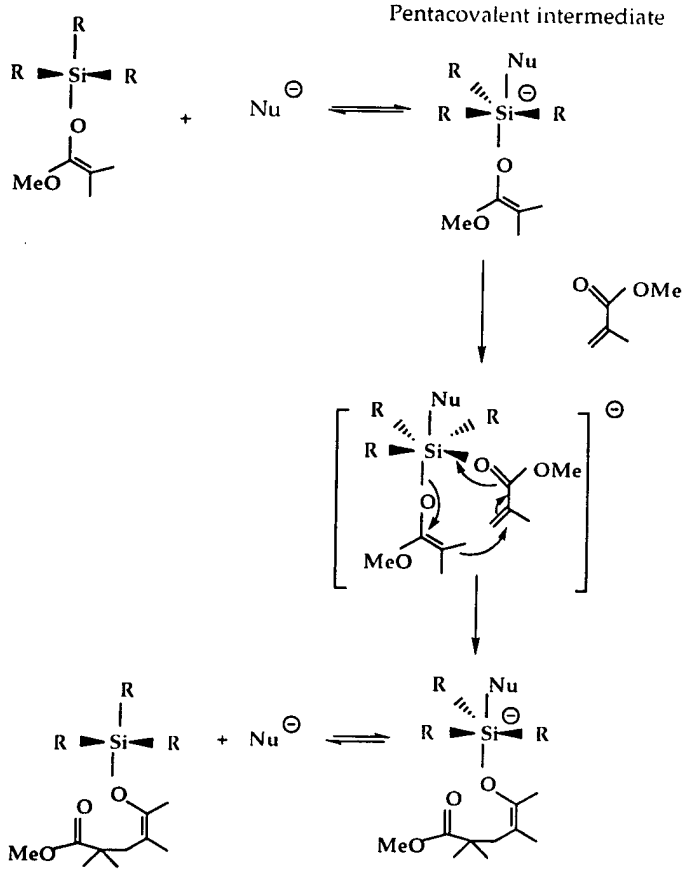
[a] Ref. 26

Scheme 1:



Tab. 1. Comparison of the tacticities of poly(methyl methacrylates) prepared in THF by GTP and anionic polymerization using different counterions (Ref. 9).

Process	Counterion	Tacticity		
		m m	m r	r r
Anionic	Cs^+	10	52	38
		10	56	34[a]
GTP	Cs^+	12	53	35
Anionic	Bu_4N^+	5	39	56
GTP	Bu_4N^+	5	42	53

[a] Ref. 26

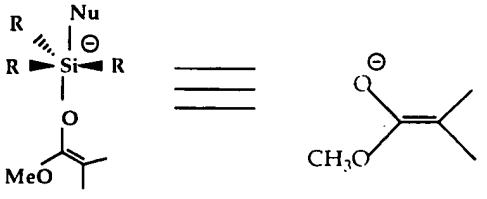
(Ref. 9). This suggests that the same types of propagating intermediates are involved in anionic polymerization and the corresponding group transfer process.

4. Very small amounts (10^{-6} moles) of ester enolate anions can function as the "nucleophilic catalyst" for living anionic GTP (Ref. 9). The proposed rapid intermolecular exchange of the nucleophilic catalyst (ester enolate anions for this system) among silyl ketene acetal chain ends, which is required to account for the observed narrow molecular weight distributions, suggests that it is not necessary to propose the existence of any other propagating intermediates other than ester enolates.

5. The monomer reactivity ratios for GTP copolymerization are similar to the monomer reactivity ratios observed for anionic polymerization (Ref.18).

6. The energies of activation and frequency factors for GTP polymerization of methyl methacrylate are very similar to the corresponding parameters for anionic polymerization (Ref. 18); it is significant to note, however, that no kinetic comparisons are available for the same counterions.

All of these experimental observations could also be interpreted as being consistent with the proposed associative GTP mechanism (Scheme 1); however, it is necessary to rationalize that the chemistry of a pentacovalent siliconate intermediate (see structure below) is essentially identical to that of an ester enolate anion intermediate. Although this is possible, it is not probable.

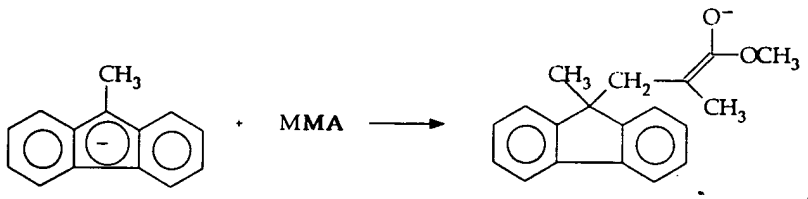


Pentacovalent intermediate Enolate

It is appropriate and prudent to critically examine what experimental evidence is available to support the associative GTP mechanism (Scheme 1). The evidence to support the associative GTP mechanism consists of :(A) the ability to carry out the living polymerization of methyl methacrylate at ambient

temperature and above; this fact stands in sharp contrast to the conditions required for living anionic polymerization of alkyl methacrylates (other than t-butyl methacrylate), e.g. -78°C (Refs. 6,7); and (B) no intermolecular silyl group exchange was reported between living oligomers in the absence or presence of polymerizing monomer as would be required by a dissociative anionic mechanism involving ester enolate anion intermediates (Refs.14,15) .

With respect to point (A) above, it has been demonstrated that anionic polymerization of methyl methacrylate (9g in 20mL of THF) at room temperature using tetrabutylammonium 9-methylfluorenide anion ($2x10^{-6}$moles) as initiator proceeds to form polymer with $\bar{M}_n$=1.3 $x10^5$ g/mol ($\bar{M}_w/\bar{M}_n$=2.0), although the yield was only 14%. It was assumed that 9-methylfluorenide reacts with methyl methacrylate to form the corresponding ester enolate anion (eq. 1) as described by Schulz and coworkers (Ref. 27). These observations demonstrate that on the

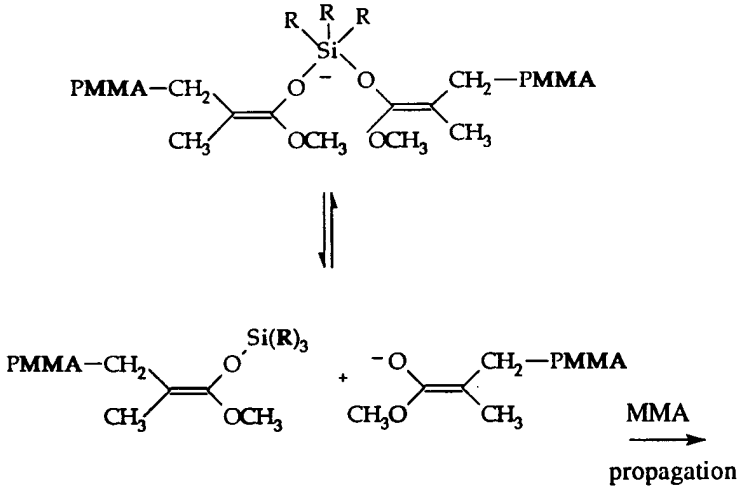


(1)

average a growing ester enolate anion can add more than 1 000 monomer units at room temperature before termination occurs. Furthermore, it has been demonstrated that this same small amount of ester enolate anion intermediate ($2 x10^{-6}$ moles) functions as the "nucleophilic catalyst" for GTP polymerization. Thus, the polymerization of methyl methacrylate (9g in 20 mL of THF) in the presence of silyl ketene acetal ($4.7 x 10^{-3}$ moles) as "initiator" and the tetrabutylammonium salt of 9-methylfluorenide ($2 x10^{-6}$ moles) as "nucleophilic catalyst" displayed all of the characteristics of a living GTP polymerization (Ref. 9). The molar mass ($\bar{M}_n$=5 $x 10^3$ g/mol; $\bar{M}_w/\bar{M}_n$ = 1.2) was controlled not by the number of moles of fluorenyl carbanion but by the number of moles of silyl ketene acetal initiator. The process was living as demonstrated by the initial preparation of a living polymer ($\bar{M}_n$= 2.2 $x10^3$ g/mol; $\bar{M}_w/\bar{M}_n$=1.2), allowing it to stand in the absence of monomer for a period of 3.75 hours, and then adding additional monomer to form a polymer with $\bar{M}_n$= 12 $x 10^3$ g/mol and $\bar{M}_w/\bar{M}_n$ = 1.1. No evidence for terminated chains with $\bar{M}_n$ corresponding to the original polymer was observed by SEC analysis. To explain the living nature of the

process for ester enolate anion intermediates as nucleophilic catalysts in the presence of silyl ketene acetal chain ends, it was proposed that the ester enolate anion intermediates are rapidly and reversibly complexed with silyl ketene acetal chain-end groups as shown in Scheme 2. This equilibrium provides a rationale

Scheme 2:



for the living nature of these polymerizations and the role of the silyl ketene acetals in controlling molecular weight. This mechanism invokes a pentacovalent intermediate not as a propagating species, but as a reservoir for the enolate anion intermediates, and the reversible formation of this intermediate provides a low equilibrium concentration of the ester enolate propagating anions.

With respect to point (B), the lack of intermolecular silyl group exchange is undoubtedly the most significant experimental evidence to support the associative GTP mechanism which explicitly states that every monomer addition is accompanied by a silyl group transfer from the silyl ketene acetal chain end of a growing polymer to the carbonyl group of the incoming monomer to form a new silyl ketene acetal chain end (The GTP Criterion) (Ref. 14,15). In spite of the importance of these exchange experiments, they have not been described in detail with experimental evidence in a refereed journal nor have they been reexamined by another laboratory until recently (Ref. 28). It is important to critically address the question of silyl group exchange in view of the experimental evidence suggesting that ester enolate anions are involved as propagating intermediates in GTP.

RESULTS AND DISCUSSION

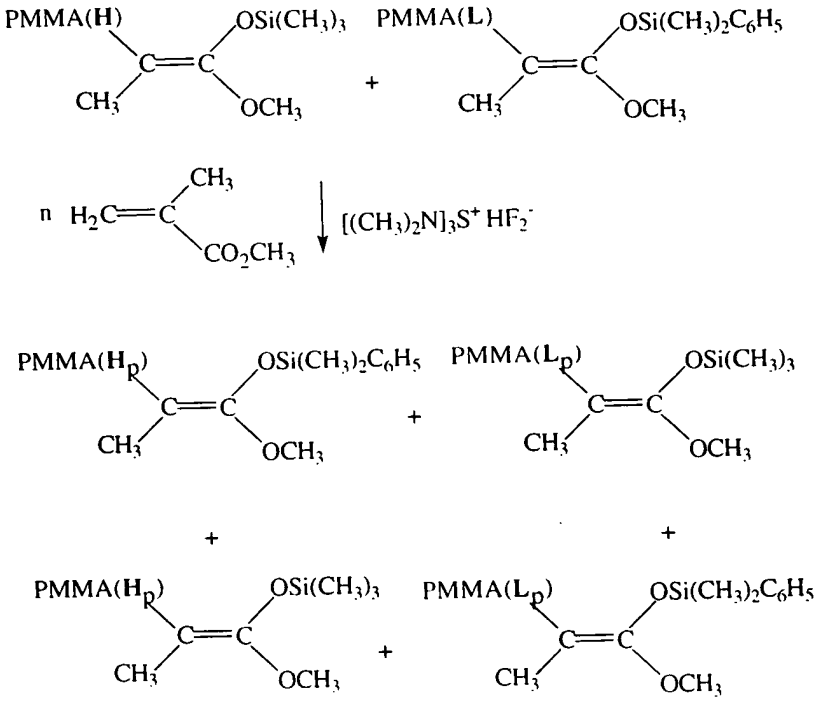
We recently undertook a detailed examination of the question of whether intermolecular silyl group exchange occurs between propagating chain ends during nucleophile-assisted group transfer polymerization (Ref. 28). Silyl group exchange was observed in all systems investigated. Thus, phenyldimethylsilyl ketene acetal initiator ($1x10^{-3}$mol) was reacted with a living trimethylsilyl-ended PMMA ($1x10^{-3}$mol, $\bar{M}_n$=$2.3x10^3$g / mol, $\bar{M}_w/\bar{M}_n$=1.06) in the presence of the *tris*(dimethylamino)sulfonium bifluoride ($TASHF_2$) catalyst ($2x10^{-5}$mol) in 20mL of THF for one hour at room temperature; ^{1}H NMR analysis of the polymeric fraction indicated 80% incorporation of the dimethylphenylsilyl group into the living polymer chains. This type of exchange was also observed by Farnham and Sogah (Refs. 14,15) in their silyl group exchange studies.

Sogah and Farnham (Ref. 15) reported that no silyl group exchange was observed when oligomers [living PMMA with a triethylsilyl ketene acetal chain end and poly(butyl methacrylate) with a trimethylsilyl ketene acetal chain end] were mixed at room temperature in the presence of $TASHF_2$ nucleophilic catalyst. Unfortunately, no experimental details were provided with which to either evaluate or reproduce these experiments. However, we have reexamined this conclusion using the simple technique of mixing living polymers of different molecular weights and with different silyl end groups in the presence of the TAS bifluoride nucleophilic catalyst, followed by separation by fractionation (Ref. 28). Living trimethylsilyl-ended PMMA ($1x10^{-3}$mol, $\bar{M}_n$=$1.3 x10^4$ g / mol; $\bar{M}_w/\bar{M}_n$=1.06) was mixed with dimethylphenylsilyl-ended PMMA ($1x10^{-3}$mol, $\bar{M}_n$=$3.1 x10^3$ g / mol; $\bar{M}_w/\bar{M}_n$=1.07) in the presence of TAS bifluoride catalyst ($2x10^{-5}$ mol) in 20mL of THF for 20 minutes. After fractionation, ^{1}H NMR analysis of both the high molecular weight and the low molecular weight fractions provided clear evidence for the incorporation of the exchanged silyl groups (40 and 72%) in the living polymer chain ends. When the labels were reversed, silyl group exchange was detected by ^{1}H NMR for both the higher (28 % exchange) and lower (27% exchange) molecular weight chains. These results are consistent with the formation of ester enolate anion intermediates when silyl ketene acetal chain ends are reacted with nucleophilic catalysts as shown in Scheme 2 and these results contradict the statement of Farnham and Sogah (Ref. 15) that no such exchange was observed between living oligomers in the presence of $TASHF_2$ nucleophilic catalyst.

A control experiment was performed to determine if exchange was occurring during the fractionation process; fractionation was carried out directly on mixtures of two living polymers. Equal numbers of moles of living trimethylsilyl-ended PMMA and dimethylphenylsilyl-ended PMMA of different molecular weights were dissolved in 20 mL of THF, and then the standard fractionation procedure was immediately carried out for the mixture. The ^1H NMR results of the high and low molecular weight fractions provided no evidence for silyl group exchange. These results showed that exchange did not occur during the fractionation process and that the chains retain their silyl ketene acetal functionality.

Farnham and Sogah (Refs. 14,15) also reported that no silyl group exchange occurred between labeled oligomers during GTP polymerization of butyl methacrylate. To provide independent experimental evidence relating to the question of whether silyl group exchange occurs during GTP polymerization, two living polymers labeled with different silyl groups and with different molecular weights were used to initiate further propagation of MMA (see Scheme 3); silver nitrate was added in order to try to reproduce some of the reported details of the exchange experiments of Sogah and Farnham (Refs. 14,15) for which no exchange was reported. It was reported that $TASHF_2$ reacts with $AgNO_3$ to form $AgHF_2$ which was not a GTP catalyst. Trimethylsilyl-ended PMMA(H) ($1x10^{-3}$ mol, $\bar{M}_n$=1.4 $x10^4$ g/mol, $\bar{M}_w/\bar{M}_n$ =1.05,) was mixed with dimethylphenylsilyl-ended PMMA(L) ($1x10^{-3}$ mol, $\bar{M}_n$=2.9 $x10^3$ g/mol, $\bar{M}_w/\bar{M}_n$ =1.05) in the presence of $TASHF_2$ catalyst ($2 x10^{-5}$ mol) in 20 mL of THF; then 9.6 g (80 % of total monomer added) of methyl methacrylate (MMA) was added dropwise over a 20 minute period. At this point, silver nitrate ($2.5x10^{-3}$ mol) was added, while continuing to add the remainder (2.4 g, 20%) of the MMA monomer. The mixture was then precipitated into petroleum ether. The ^1H NMR spectra of the fractionated polymers once again provided clear evidence for silyl group exchange in both the high molecular weight fraction (H_p)(44% exchange) [δ=0.38 ppm for Ø($C\underline{H}_3$)$_2$-Si] and the low molecular weight fraction (H_p) (38% exchange) [δ=0.05 ppm for ($C\underline{H}_3$)$_3$-Si] . Thus, significant amounts (38-44%) of silyl group exchange occur readily between living polymer chains under GTP polymerization conditions in the presence of

Scheme 3: (**H** refers to high molar mass; **L** refers to low molar mass; and $\mathbf{H_p}$ and $\mathbf{L_p}$ are polymers which have exchanged silyl groups)



polymerizing monomer in contrast to previous preliminary reports and conclusions (Refs. 14,15).

The silyl group exchange experiments of Sogah and Farnham (Refs. 14,15) were carried out between dimethyltolylsilyl-ended PMMA and dimethylphenylsilyl-ended poly(butyl methacrylate) (PBMA) in the presence of excess butyl methacrylate by adding all of the monomer at once and quenching at 70% conversion; it was reported that under these conditions, no detectable silyl group exchange was observed. Since the polymers were separated based on the solubility differences between PMMA and PBMA, the incompatibility of these different polymers may have favored silyl exchange between like polymer chains with the same silyl groups; thus, silyl group exchange would not be detected (Ref. 29). This is one possible explanation for the disparity between the preliminary results reported by Farnham and Sogah (Refs. 14,15), which indicated that no silyl group exchange occurs, and our observations of significant silyl group exchange

during GTP polymerization.

Another possible explanation for the observation of silyl group exchange as discussed herein (Ref. 28) and the lack of exchange reported previously (Refs. 14,15) would be that silyl group exchange is a slow side reaction which does not compete with the rapid propagation reaction involving intramolecular silyl group transfer. This is the rationalization which was advanced previously to reconcile the observation that although silyl group exchange was observed between living oligomers and silyl ketene acetal initiators, no intermolecular silyl group exchange was observed between living oligomers in the presence or absence of polymerizing monomer (Ref. 15). However, we have observed intermolecular silyl group exchange both in the presence and absence of polymerizing monomer (Ref. 28). We observed exchange between living oligomers (20 minute reaction time) in all systems investigated, in both the high and the low molecular weight fractions, and with the silyl labels reversed. No experimental details were provided for the previous work (ref. 15), so that it is possible that the time period allowed for exchange was very short (e.g. only a few minutes). Thus, the argument could be advanced that our observed exchange reaction is slow relative to the known fast rate of polymerization. The discrepancy between our exchange results and previous work for living oligomers in the presence of polymerizing monomer can be rationalized using a similar argument. Thus, in the exchange studies of Farnham and Sogah (Refs. 14,15), all of the monomer was present initially, propagation of butyl methacrylate occurred (70%) and the polymerization was quenched after a period of several minutes; no evidence for silyl group transfer was reported. In contrast, our observed silyl group exchange studies were carried out by continuous monomer addition, i.e. under monomer-starved conditions. It can be argued that the observed silyl group exchange is slow relative to propagation and was only observed because of the experimental conditions of slow monomer addition.

Although the above arguments can be advanced to reconcile our observed silyl group exchange results with the associative mechanism for GTP , several factors tend to mitigate against this explanation. First, since very low amounts of ester enolate anions (10^{-6} moles) can serve as nucleophilic catalysts for GTP and the resulting polymerization is living for periods of at least 3.75 hours (Ref.9), the formation of very small amounts of ester enolate anions is all that is required to be consistent with an enolate anion propagating reaction. Thus, if ester enolate anion formation is a side reaction, it is necessary to propose that less than 10^{-6} moles of ester enolate anions are formed in the presence of

polymerizing monomer. Furthermore, our exchange experiments were carried out under typical GTP polymerization conditions, i.e. continuous monomer addition to control the exothermic polymerization. The conclusion that this is not mechanistically significant implies that under these conditions there are side reactions involving ester enolate anions which are favored relative to the pure associative mechanism of propagation. The fact that these polymerizations are living and produce well defined polymers contradicts this argument. The small amount of ester enolate anion which will catalyze silyl group exchange is also the same small amount which serves as the nucleophilic catalyst for polymerization.

The fact that such small amounts of the ester enolate anions serve as the nucleophilic catalyst for GTP, the fact that rapid exchange of the nucleophile between chains is required to explain the relatively narrow molecular weight distributions observed in GTP, and the fact that ester enolate anions can certainly add monomer, all suggest that it is not necessary to propose that any other species (e.g., pentacovalent siliconate intermediate) is involved in the propagation reaction. Finally, one can add the observation of significant intermolecular silyl group exchange, as predicted by the proposal that ester enolate anions are "nucleophilic catalysts" and propagating species, and in contradiction to the GTP Criterion, to the growing body of evidence which is consistent with ester enolate anions as the propagating intermediates in GTP polymerization. In contrast, the continuing advocacy of the associative mechanism for GTP requires (A) the postulate that the chemistry of a pentacovalent siliconate intermediate is essentially identical to that of an ester enolate anion intermediate; (B) the belief that the as yet unpublished and unrefereed experiments which purport to show the absence of silyl group exchange between living oligomers in the presence and absence of polymerizing monomer are correct and can be interpreted unambiguously (Refs. 14,15); and (C) that the observed intermolecular silyl group exchange reactions reported in detail for living oligomers in the presence and absence of polymerizing monomer (Ref. 28) are not mechanistically significant.

CONCLUSIONS

The experimental evidence to support the associative mechanism proposed for group transfer polymerization was based on the GTP Criterion which states that "in this associative mechanism, silyl exchange among growing chains is excluded: the identity of the silicon atom of the initiator molecule remains invariant throughout the growth of the polymer chains" (Refs. 14,15). As a direct test of this mechanism using the GTP Criterion, silyl group exchange experiments show that significant amounts of silyl group exchange occur during typical GTP polymerization conditions (gradual monomer addition). It is concluded that silyl

group exchange is occurring in GTP polymerization and that this experimental evidence is not in accord with the associative mechanism but it is consistent with ester enolate anions as propagating species.

ACKNOWLEDGEMENT

The authors are grateful to the B.F. Goodrich Company for support of this research in the form of an Enhanced Fellowship to J.R.

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